4.1 Introduction

The overall geochemical processes prevailing in estuaries cannot be explained by mere application of geochemical parameters such as total content of organic matter, chemo-dynamics of P and total concentrations of sedimentary trace metals. The redox status of sedimentary environment in estuaries is directly linked to the processes of organic matter remineralisation. Organic matter remineralisation regenerate nutrients in the sediment and the regenerated nutrients diffuse or transport back to the overlying water and support water column production (Dunn et al., 2008). The biogeochemical processes associated with organic matter remineralisation are not a simple function of the total quantity of organic matter present, but also depends on the quality of organic matter. Therefore, the assessment of nature and quality of organic matter is of prime importance for explaining organic matter remineralisation. The biochemical composition of sedimentary organic matter has been employed to gather information on the
nature and parameters controlling the diagenetic fate of organic matter. The concentrations of labile organic biopolymers (proteins, carbohydrates, lipids and chlorophyll pigments) are considered as best tool for the evaluation of nature and quality of organic matter which can provide clear insights into the biogeochemical characterisation of sedimentary environment in estuaries (Colombo, 1996; Dell’ Anno et al., 2002; Pusceddu et al., 2009, 2011; Venturini et al., 2012).

4.2 Biochemical Composition of Organic Matter

Sedimentary organic matter in estuaries is composed of complex mixture of organic molecules characterised by large variability in composition and reactivity (Middelburg and Herman, 2007). Nature and quality of organic matter largely depend on several factors including origin, composition and biochemical transformations that occur on organic particles during their descent through the water column (Cowie and Hedges, 1992). Sedimentary organic matter comprises labile and refractory organic compounds, whose abundance changes as a function of complex array of processes including degradation, heterotrophic utilisation, transformation and export (Viollier et al., 2003; Venturini et al., 2012). Refractory organic compounds include fulvic acids, humic acids and structural carbohydrates which are characterised by lower degradation and high preservation in sediments (Middleburg et al., 1999; Danovaro et al., 1999). The labile fraction of sedimentary organic matter consists of simple and/or combined organic biopolymer molecules such as proteins, carbohydrates and lipids, which are available for benthic organisms and rapidly mineralised (Venturini et al., 2012). The production or inputs of rapidly sinking particles allows the accumulation of organic materials, which have suffered a continuous process of degradation of labile
compounds in the water column. Even after sedimentation, organic particles are equally subjected to continuous degradation and mixing process (Colombo, 1996; Cotano and Villate, 2006).

The labile organic compounds in sediments represent the fraction of organic matter available to the benthic community (Mayer et al. 1995). The biopolymeric carbon (BPC) fraction of sedimentary organic matter, calculated by sum of protein, carbohydrate and lipid carbon has been reported as the fraction of total organic carbon potentially available to the benthic consumers (Pusceddu et al., 2009). Organic biochemical components vary faster than the more conservative total organic carbon in response to spatial and temporal changes in the benthic trophic status associated to both natural and human-induced environmental alterations (Dell’Anno et al., 2002; Pusceddu et al., 2003, 2009; Joseph et al., 2008).

4.3 Chlorophyll Pigments in Sedimentary Organic matter

Chlorophyll pigments are abundant in estuarine environment and are recognised as markers of different processes taking place in the sea water and sediments (Szymczak-Zyła and Kowalewska, 2007). Pigments are useful as molecular biomarkers due to their taxonomic specificity and hold the potential to represent the entire phototrophic community and overall primary production. The comparative labiality and source specificity of pigments makes them a powerful tool to investigate many aspects of biogeochemical processes as well as organic matter source and history (Sun and Dai, 2005; Reuss, 2005). Sedimentary pigments can provide information on various aspects of benthic processes and biogeochemistry (Woulds and Cowie, 2009). Only a fraction of photosynthetic production from water column end up in sediment surface and the most extensive
degradation of pigments take place during the deposition through the water column in the surface sediments (Cuddington and Leavitt, 1999). Oxygen concentration in sediment water interface greatly influences the pigment preservation in sediment (Sun et al., 1993).

4.4 Bulk Organic Matter Techniques

Determining the relative contribution of organic matter fuelling the biogeochemical processes in estuarine sediments remains a challenge due to the wide range of organic matter sources in estuaries as well as the spatio-temporal variations in the delivery of organic matter to the sediments. In recent years, the source characterisation of sedimentary organic matter is achieved by using combination of bulk indices (C/N ratios and δ\(^{13}\)C and δ\(^{15}\)N) and molecular biomarkers. The bulk elemental and isotopic approach is based on the following two assumptions: i) the bulk elemental and isotopic ratios of sedimentary organic matter are conservative and ii) there exist a linear response to physical mixing among the end members (Liu et al., 2006; Rumolo et al., 2011).

Most of the photosynthetic organisms including trees, shrubs, phytoplankton etc. incorporate carbon into their biomass using the Calvin (C\(_3\)) pathway which discriminates against \(^{13}\)C to produce a shift in δ\(^{13}\)C values of about -20‰ from the isotopic ratios of inorganic carbon source. Some plants (many subtropical savannah grasses and sedges) use the Hatch-Slack pathway (C\(_4\)) which leads to an isotopic shift of -7‰ from the inorganic carbon source. Other plants mostly succulents, utilise the Crassulacean Acid Metabolism (CAM) which more or less switches between the C\(_3\) and C\(_4\) pathway and causes the δ\(^{13}\)C values to depend on growth dynamics (Schulz and Zabel, 2006). Terrestrial organic matter
produced by C$_3$ pathway have $\delta^{13}$C values ranging from -30 to -26‰, while for C$_4$ pathway it is from -16 to -9‰ (Pancost and Boot, 2004). Simultaneous utilisation of bulk elemental and isotopic parameters helps to obtain an improved identification of source as well as fate of organic matter in estuarine sediments. The usefulness of OC/N, $\delta^{13}$C and $\delta^{15}$N relies on the fact that there exist characteristic source specific bulk elemental and isotopic signatures for terrigenous, anthropogenic, marine and in situ organic matter.

Organic detritus in sedimentary organic matter pool has long been recognised for its influence on the biogeochemical cycles of both water column and sediments and its importance as a benthic food resource (Mann and Lazier, 1991; Bianchi and Bauer, 2011). The organic detritus comprises planktonic materials, animal faecal pellets and vascular materials which exhibit different reactivity to leaching and remineralisation processes. The relative contribution of different sources of detritus will affect the biogeochemical cycling of organic matter. Hence, a vivid knowledge about the nature, quality and the relative contribution of different sources (e.g. planktonic vs. terrestrial plant materials) is of prime importance for understanding organic matter dynamics in estuaries. This chapter investigates the nature and quality of organic matter in surface sediments of Cochin estuary and evaluates the relative contribution of different sources of sedimentary organic matter by the application of bulk organic matter techniques and chlorophyll pigment distributions.

4.5 Results

4.5.1 Biochemical Composition of Sedimentary Organic Matter

TOM concentrations in the sediments varied from 1.24 to 6.15% (3.98±1.82), 0.54 to 5.77% (3.33±1.93) and 0.65 to 5.39% (3.33±1.64)
during the monsoon, post-monsoon and pre-monsoon seasons respectively. TOM showed a decreasing trend from seaward to Thanneermukkom bund and remarkably high concentrations were recorded at stations S1 to S7. The spatial and seasonal distributions of biochemical components are presented in Fig. 4.1. PRT concentrations in the sediments ranged from 1.40 to 7.3mg g⁻¹ (4.79±1.77), 1.09 to 12.33mg g⁻¹ (5.30±3.03) and 0.51 and 9.67mg g⁻¹ (4.27±2.57) during the monsoon, post monsoon and pre monsoon seasons respectively. Higher PRT concentrations were found during the post monsoon when compared with the monsoon and pre monsoon seasons. CHO concentrations in the sediments ranged from 4.17 to 14.00mg g⁻¹ (8.42±3.19), 2.21 to 5.66mg g⁻¹ (8.34±4.30) and 0.87 to 9.02mg g⁻¹ (5.70±2.53) during the monsoon, post monsoon and pre monsoon seasons respectively. LIP concentrations in the sediments ranged from 0.01 to 1.50mg g⁻¹ (0.81±0.46), 0.13 to 0.93mg g⁻¹ (0.51±0.28) and 0.05 to 1.99mg g⁻¹ (0.93±0.64) during the monsoon, post monsoon and pre monsoon seasons respectively. BPC concentrations in the sediments ranged from 0.25 to 0.96% (0.6±0.23), 0.16 to 1.25% (0.63±32) and 0.06 to 0.79% (0.50±0.24) during the monsoon, post monsoon and pre monsoon seasons respectively.

Carbohydrates in the sediments represent a major biochemical class (BPC pools) of organic compounds during the monsoon (53.45 %), post monsoon (53.15 %) and pre monsoon (46.95 %) respectively. This is followed by proteins monsoon (37.41 %), post monsoon (40.53 %) and pre monsoon (40.23 %) and lipids monsoon (8.74 %), post monsoon (6.31 %) and pre-monsoon (12.83 %).
The spatial and seasonal variations in Chl-$a$ and Pheo are presented in Fig.4.2. Chl-$a$ concentrations in the surface sediments ranged from 0.37 to 7.20 $\mu g g^{-1}$ (2.29±1.89), 5.72 to 18.62 $\mu g g^{-1}$ (10.02±4.97) and 0.02 to 17.91 $\mu g g^{-1}$ (6.26±3.88) in monsoon, post monsoon and pre monsoon seasons respectively. Maximum Chl-$a$ concentration was recorded at station 5 during the post monsoon season, while the lowest concentration was observed at S1 during the pre monsoon season. Chl-$b$ concentrations ranged from 0.05 to 6.13 $\mu g g^{-1}$ in monsoon, 0.09 to 5.73 $\mu g g^{-1}$ in post monsoon and 0.08 to 3.85 $\mu g g^{-1}$ in pre monsoon. Chl-$c$ displayed comparatively lower concentrations in the study region which ranged from n.d to 7.20 $\mu g g^{-1}$ in monsoon, n.d to 4.85 $\mu g g^{-1}$ in post monsoon and n.d to 3.44 $\mu g g^{-1}$ in pre monsoon season. Pheo concentrations in the sediments ranged from 0.52 to 52.71 $\mu g g^{-1}$ (16.81±14.01), 7.59 to 46.65 $\mu g g^{-1}$ (23.46±12.76) and 2.14...
to 26.90µg g⁻¹(15.86±8.22) in monsoon, post monsoon and pre monsoon seasons respectively. Highest Pheo concentration was recorded at S5 in monsoon season, while the lowest recorded at S12 at monsoon season.

From the results it was found that Chl-α concentrations displayed highly significant seasonal variations (p<0.001) in the study region but lack significant differences along the sampling sites. Comparatively higher Chl-α concentrations were observed in post monsoon, while lower values were observed in monsoon season. However, Chl-β concentrations did not display any seasonal variations but it showed differences among the sampling sites (p<0.01). Pheo did not display any spatial and seasonal variations in the study region.
The results of correlation analysis of sedimentary biogeochemical parameters are presented in Table 4.1. All biogeochemical parameters (except Chl-\(a\) and Pheo) showed highly significant positive correlation with clay and silt content and negative correlation with sand, which indicated that the sediment texture is one of the main factors influencing organic matter accumulation in the study region. This phenomenon is ascribed to the close hydraulic equivalence of both organic and mud particles and/or to the relatively high absorptive capacity of fine particles for organic molecules (Cotano and Villate, 2006). OC, TN and TS also displayed significant positive correlation with the biochemical components in the surface sediments.

All the sedimentary parameters, both geochemical and biochemical showed a significant spatial variation (ANOVA \(p<0.05\)) except Chl-\(a\) and pheopigments (Table 4.2). Sediment texture displayed more significant spatial variations than seasonal variations. BPC and TN also showed significant spatial variation. Chl-\(a\) concentrations exhibited significant seasonal variation, but have not displayed any significant spatial variations. CHO was characterized with significant spatial and seasonal variations with the highest concentrations during the monsoon and lowest concentrations in the pre-monsoon seasons. Seasonal variations of LPD and PRT concentrations showed opposite trends. While pre-monsoon was characterized with a higher LIP and lower PRT concentrations, pre monsoon was characterized with a lower LIP and higher PRT concentrations.
Table 4.1 Pearson correlation between sedimentary parameters in the Cochin Estuarine System (n = 42).

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>OC</th>
<th>TN</th>
<th>TS</th>
<th>Chl-α</th>
<th>Pheo</th>
<th>PRT</th>
<th>TCHO</th>
<th>LPD</th>
<th>BPC</th>
</tr>
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<tbody>
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<td></td>
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<td></td>
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<tr>
<td>Silt</td>
<td>-0.84**</td>
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<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Clay</td>
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<tr>
<td>TOM</td>
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<td>0.63**</td>
<td>0.74**</td>
<td>1</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>TN</td>
<td>-0.83**</td>
<td>0.62**</td>
<td>0.69**</td>
<td>0.91**</td>
<td>1</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>TS</td>
<td>-0.85**</td>
<td>0.61**</td>
<td>0.74**</td>
<td>0.90**</td>
<td>0.89**</td>
<td>1</td>
<td></td>
<td></td>
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<tr>
<td>Chl-α</td>
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<td>-0.23</td>
<td>0.51**</td>
<td>0.19</td>
<td>0.23</td>
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<td>1</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pheo</td>
<td>-0.12</td>
<td>-0.14</td>
<td>0.40**</td>
<td>0.24</td>
<td>0.31*</td>
<td>0.23</td>
<td>0.75**</td>
<td>1</td>
<td></td>
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</tr>
<tr>
<td>PRT</td>
<td>-0.65**</td>
<td>0.39*</td>
<td>0.66**</td>
<td>0.78**</td>
<td>0.77**</td>
<td>0.69**</td>
<td>0.32*</td>
<td>0.33*</td>
<td>1</td>
<td></td>
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<tr>
<td>CHO</td>
<td>-0.73**</td>
<td>0.55**</td>
<td>0.60**</td>
<td>0.89**</td>
<td>0.81**</td>
<td>0.79**</td>
<td>0.16</td>
<td>0.21</td>
<td>0.75**</td>
<td>1</td>
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<td></td>
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<tr>
<td>LPD</td>
<td>-0.69**</td>
<td>0.58**</td>
<td>0.50**</td>
<td>0.59**</td>
<td>0.71**</td>
<td>0.66**</td>
<td>0.08</td>
<td>0.06</td>
<td>0.51*</td>
<td>0.46**</td>
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</tr>
<tr>
<td>BPC</td>
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<td>0.69**</td>
<td>0.90**</td>
<td>0.88**</td>
<td>0.82**</td>
<td>0.24</td>
<td>0.27</td>
<td>0.92**</td>
<td>0.93**</td>
<td>0.62**</td>
<td>1</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed)
Quality and Sources of Sedimentary Organic Matter

Table 4.2 The mean values of different biogeochemical parameters measured in the surface sediments of Cochin estuary and the result of ANOVA of different biogeochemical variables.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean</th>
<th>Source of variation</th>
<th>df</th>
<th>F</th>
<th>p value</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Mon</td>
<td>Post</td>
<td>Pre</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OC (%)</td>
<td>2.21</td>
<td>1.85</td>
<td>1.85</td>
<td>Stations</td>
<td>13</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
</tr>
<tr>
<td>TN (%)</td>
<td>0.2</td>
<td>0.17</td>
<td>0.18</td>
<td>Stations</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
</tr>
<tr>
<td>TS (%)</td>
<td>0.69</td>
<td>0.6</td>
<td>0.57</td>
<td>Stations</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
</tr>
<tr>
<td>Chl-a (µg g⁻¹)</td>
<td>2.29</td>
<td>10.02</td>
<td>6.26</td>
<td>Stations</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
</tr>
<tr>
<td>Pheo (µg g⁻¹)</td>
<td>16.81</td>
<td>23.46</td>
<td>15.86</td>
<td>Stations</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
</tr>
<tr>
<td>PRT (mg g⁻¹)</td>
<td>7.31</td>
<td>12.33</td>
<td>9.67</td>
<td>Stations</td>
<td>13</td>
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<td></td>
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<td>Seasons</td>
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<tr>
<td>CHO (mg g⁻¹)</td>
<td>8.42</td>
<td>8.34</td>
<td>5.7</td>
<td>Stations</td>
<td>13</td>
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<td></td>
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<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
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<tr>
<td>LPD (mg g⁻¹)</td>
<td>0.81</td>
<td>0.51</td>
<td>0.93</td>
<td>Stations</td>
<td>13</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
</tr>
<tr>
<td>BPC (%)</td>
<td>0.63</td>
<td>0.63</td>
<td>0.51</td>
<td>Stations</td>
<td>13</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>Seasons</td>
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<tr>
<td>PRT/CHO</td>
<td>0.59</td>
<td>0.64</td>
<td>0.75</td>
<td>Stations</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seasons</td>
<td>2</td>
</tr>
</tbody>
</table>

**significant at the 0.01 level, *significant at the 0.05 level, ns- not significant.

4.5.2 Bulk elemental and isotopic ratios

Fig. 4.3 shows the spatial and seasonal variability of OC and TN in surface sediments of Cochin estuary. The OC concentrations ranged from 0.85 to 3.26% (2.28±0.94) in monsoon, 0.30 to 3.03% (2.11±1.02) in post monsoon and 0.62 to 2.74% (1.91±0.81) in pre monsoon season. The spatial distribution of OC indicated that OC content is comparatively high.
at stations S1, S2, S3, S4 and S6 than the other stations. However, it was observed that there is no significant seasonal difference in OC content of surface sediments. Concentrations of TN were relatively lower in surface sediments of Cochin estuary, which varied from 0.07 to 0.31% (0.20±0.10), 0.03 to 0.32% (0.19±0.10) and 0.09 to 0.25% (0.18±0.06) in monsoon, post monsoon and pre monsoon respectively. TN varied significantly among the sampling sites, but it did not display any seasonal difference. The spatial and seasonal variations of TN are similar to OC.

The spatiotemporal variation in $\delta^{13}$C and $\delta^{15}$N values in surface sediments is presented in Fig.4.3. The $\delta^{13}$C in surface sediment of Cochin estuary ranged from -25.8 to -22.8‰ in monsoon, -27.0 to -22.4‰ in post monsoon and -27.5 to -21.7‰ in pre monsoon. $\delta^{13}$C showed a clear spatial
gradient with higher values towards the seaward side, while it lacks seasonal variation. There was an increasing heavier trend in $\delta^{13}C$ values at the gradient of increasing salinity in the overlying waters. The $\delta^{15}N$ values in the surface sediment varied from 4 to 6.4‰, 3.9 to 6.3‰ and 3.1 to 6.7‰ in monsoon, post monsoon and pre monsoon respectively. $\delta^{15}N$ did not display any spatial or seasonal variations.

4.6 Discussion

There is scarce information in literature about the biochemical compounds in sediments of the Cochin estuary. Biochemical composition of sedimentary organic matter in the mangrove ecosystems of the northern part of the Cochin estuary were studied by Joseph et al., 2008 and the observations in the present study are well within the ranges reported therein. The contribution of labile organic matter to total organic matter pool was very high in most stations.

CHO dominated among the organic biopolymers in the study region and the observed concentrations are compared with those reported in other eutrophic systems. The rampant propagation of water hyacinth during the monsoon and post monsoon season is a major ecological problem in the Cochin estuary. Comparatively higher concentration of CHO may be attributed to decay and decomposition of these floating plants in the estuary. High levels of CHO concentrations in surface sediments have also been attributed to the accumulation of aged organic detritus due to the faster utilisation of proteins than carbohydrates by micro organisms (Joseph et al., 2008; Venturini et al., 2012).

The PRT concentrations found in the present study were comparable to those reported in other eutrophic systems (Dell’Anno et al., 2002; Cotano and...
A number of fish peeling and processing units are situated in the banks of the Cochin estuary. The wastes from these units are dumped into the estuary where tissues undergo decomposition to liberate protein, which are finally adsorbed/settled into the surface sediments (Vasudevan, 2000; Balasubramaniam et al., 2012). PRT/CHO ratio > 1 has been attributed to the presence of fresh materials of recent origin, while PRT/CHO ratio <1 indicated to the predominance of aged organic matter in surface sediments (Danovaro et al., 1993). The PRT/CHO ratio remained <1 (Fig.4.4) in almost all stations during the study which implies the accumulation of more degraded organic matter in the estuarine sediments.

The LIP values obtained in the present study were in good agreement with those reported for Bilbao estuary, Spain (0.97-2.5mg g⁻¹), Ligurian sea, Italy (1.0-1.4mg g⁻¹) (Cotano and Villate, 2006) and lower than those reported Rio de la Plata estuary, Uruguay (1.12-6.63 mg g⁻¹) (Venturini et al., 2012). Cochin estuary houses the 4th largest port in India and this facility currently handles export and import of container cargos (1225 vessels, 13.9 × 10⁶ tons during 2005-06) at its terminal at the Willingdon
Island (Martin et al., 2012). Comparatively high LIP concentrations at stations around Cochin harbour region could be ascribed to anthropogenic inputs such as domestic sewage inputs from Cochin City and petroleum inputs. Usually high LIP values have been reported from many industrialised and urbanised estuaries because the method used to extract lipids may also recover significant quantities of organic contaminants such as hydrocarbons reflecting high degree of pollution (Galois et al., 2000; Venturini et al., 2012).

4.6.1 Benthic Trophic Status

Basic studies on the assessment of trophic status have been based on the measurement of physical, chemical and biological measurement of water column variables such as water column turbidity, inorganic nutrients (predictive variables) and Chl-α (responsive variables) concentrations (Zurlini, 1996; Cloern, 2001; Coelho et al., 2007). Many authors reported that the measurements of these predictive and responsive variables are insufficient to provide better insights into the trophic status of aquatic ecosystems (Izzo et al., 1997; Cognetti, 2001; Dell’Anno et al., 2002; Pusceddu et al., 2011). In shallow ecosystems like estuaries, ponds and lagoons, there is a significant contribution of Chl-α from microphytobenthose and macroalgae to benthic primary production (Dell’Anno et al. 2002). The re-suspension events in these shallow ecosystems might lead to an increased concentration of Chl-α in water column, thereby creating discrepancies in the assessment of trophic status (Conde et al. 1999; Pusceddu et al. 1999). Since these predictive and responsive variables are ineffective in shallow coastal systems, Nixon (1995) proposed a new approach for the assessment of trophic status based on the supply of total organic carbon in terms of gCm⁻²y⁻¹. Even though this approach moves
focus on the potential consequence of eutrophication in the benthic realm, it showed poor sensitivity because it does not consider the differential reactivity of wide range of organic compounds within the sediments (Pusceddu et al., 2009).

The benthic trophic status of sampling stations were established based on PRT and CHO threshold levels proposed by Dell’Anno et al., 2002 (Hypertrophic (H): PRT>4 and CHO > 7mgg⁻¹, eutrophic (E): PRT 1.5-4mgg⁻¹ and CHO = 5.7mgg⁻¹ Meso-oligotrophic (MO): PRT<1.5mgg⁻¹ and CHO <5mgg⁻¹). BPC and algal contribution to BPC (CChl-a) levels as proposed by Pusceddu et al., 2011 (eutrophic- BPC >3 mg g⁻¹ and algal contribution to BPC <12%) are also used in this study. The benthic trophic classifications of the stations are presented in Table 4.3. Most of the stations are classified as hypertrophic using PRT threshold levels, while CHO concentrations reflect hypertrophic conditions around Cochin harbour region and meso-oligotrophic conditions in the inner part of the estuary. BPC and algal contribution to BPC are the reflection of the eutrophic conditions prevailing in the estuary.

The trophic classifications of the stations in the Cochin estuary based on the threshold values proposed by Dell’Anno et al., 2002 are presented in Table 4.3. Based on the CHO concentrations stations S3, S4, S5, S6 and S8 were classified as hypertrophic, whereas the stations S2, S7, S10 and S12 presented CHO concentrations close to eutrophic conditions. The bar mouth region and southern end of the study area (Thanneermukkom bund region) showed lower CHO concentrations reflecting meso-oligotrophic conditions. Almost the entire study region showed PRT concentrations higher than threshold values for hypertrophic conditions, while the BPC results suggested eutrophic conditions. An algal contribution to BPC <12%
indicate eutrophic conditions and lower values between 3 and 6 indicate hypertrophic conditions (Pusceddu et al., 2011). From the results it was clear that Cochin harbour region has lower algal contribution to BPC reflecting hypertrophic condition in that region, while eutrophic conditions were obtained towards the inner part of the estuary. From the above discussion it is obvious that different biochemical descriptors inferred different trophic conditions for the study area, hence a detailed examination is needed for assessing the applicability of these biochemical descriptors in the tropical estuarine and coastal systems. However, high BPC and PRT values and lower algal contribution to BPC indicate high degree of benthic eutrophication in the Cochin estuary.

Table 4.3 Benthic trophic classifications of sampling sites

<table>
<thead>
<tr>
<th>Stations</th>
<th>PRT (mgg⁻¹)</th>
<th>Trophic Status</th>
<th>CHO (mgg⁻¹)</th>
<th>Trophic Status</th>
<th>BPC (mgg⁻¹)</th>
<th>Trophic Status</th>
<th>CChl-a (%)</th>
<th>Trophic Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2.97</td>
<td>E</td>
<td>0.87</td>
<td>MO</td>
<td>5.90</td>
<td>E</td>
<td>1.38</td>
<td>H</td>
</tr>
<tr>
<td>S2</td>
<td>6.67</td>
<td>H</td>
<td>6.05</td>
<td>E</td>
<td>6.01</td>
<td>E</td>
<td>2.62</td>
<td>H</td>
</tr>
<tr>
<td>S3</td>
<td>8.10</td>
<td>H</td>
<td>9.02</td>
<td>H</td>
<td>5.81</td>
<td>E</td>
<td>2.90</td>
<td>H</td>
</tr>
<tr>
<td>S4</td>
<td>6.55</td>
<td>H</td>
<td>7.66</td>
<td>H</td>
<td>5.46</td>
<td>E</td>
<td>4.60</td>
<td>H</td>
</tr>
<tr>
<td>S5</td>
<td>6.10</td>
<td>H</td>
<td>8.14</td>
<td>H</td>
<td>5.21</td>
<td>E</td>
<td>6.15</td>
<td>E</td>
</tr>
<tr>
<td>S6</td>
<td>2.64</td>
<td>H</td>
<td>7.60</td>
<td>H</td>
<td>4.98</td>
<td>E</td>
<td>6.81</td>
<td>E</td>
</tr>
<tr>
<td>S7</td>
<td>5.81</td>
<td>H</td>
<td>6.97</td>
<td>E</td>
<td>5.13</td>
<td>E</td>
<td>3.59</td>
<td>H</td>
</tr>
<tr>
<td>S8</td>
<td>4.82</td>
<td>H</td>
<td>7.91</td>
<td>H</td>
<td>4.71</td>
<td>E</td>
<td>6.23</td>
<td>E</td>
</tr>
<tr>
<td>S9</td>
<td>3.37</td>
<td>H</td>
<td>4.94</td>
<td>MO</td>
<td>4.49</td>
<td>E</td>
<td>6.46</td>
<td>E</td>
</tr>
<tr>
<td>S10</td>
<td>5.99</td>
<td>H</td>
<td>6.58</td>
<td>E</td>
<td>4.60</td>
<td>E</td>
<td>4.95</td>
<td>E</td>
</tr>
<tr>
<td>S11</td>
<td>3.75</td>
<td>H</td>
<td>1.86</td>
<td>MO</td>
<td>4.39</td>
<td>E</td>
<td>5.07</td>
<td>E</td>
</tr>
<tr>
<td>S12</td>
<td>3.25</td>
<td>H</td>
<td>5.81</td>
<td>E</td>
<td>4.28</td>
<td>E</td>
<td>2.61</td>
<td>H</td>
</tr>
<tr>
<td>S13</td>
<td>2.13</td>
<td>H</td>
<td>3.14</td>
<td>MO</td>
<td>4.35</td>
<td>E</td>
<td>8.96</td>
<td>E</td>
</tr>
<tr>
<td>S14</td>
<td>4.90</td>
<td>H</td>
<td>3.23</td>
<td>MO</td>
<td>5.97</td>
<td>E</td>
<td>4.51</td>
<td>E</td>
</tr>
</tbody>
</table>

The Chl-α/Pheo (<1) and CChl-α (<12) indicated the enrichment of degraded phytodetritus as well as refractory organic materials in the sediments. Many previous studies demonstrated that eutrophic systems have a tendency to accumulate refractory organic matter (Pusceddu et al., 2009; Pusceddu
et al., 2011; Venturini et al., 2012) and the present study agrees well with these concepts. Management strategies should be developed to reduce the organic matter load reaching the Cochin estuary.

The influx of large amount of allochthonous organic matter into the Cochin estuary was previously reported by many authors (Saraladevi et al., 1983; Thomson, 2002; Balachandran et al., 2003; Babu et al., 2006; Thottathil et al., 2008; Martin et al., 2010). The estuary receives heavy freshwater influx during summer monsoon (June-September) when 71% of annual rainfall occurs (Srinivas et al., 2003) transporting large amount of organic matter to this estuary (Balachandran et al., 2003). Very high concentrations of dissolved organic carbon and particulate organic carbon were reported from central estuary (Martin et al., 2010) which clearly indicates that a significant portion of organic matter is derived from sewage generated from Cochin metropolitan city. The southernmost part of the estuary receives organic wastes from aquaculture fields (62km²), agricultural fields (80km²) and coconut retting yards which increase the organic pollution in an alarming rate (Thomson, 2002; Babu et al., 2006; Martin et al., 2010). All these activities lead to changes in trophic structure and have affected the functioning of this vital ecosystem. Eutrophication induced changes in benthic community structure was recently reported by Martin et al., 2011. Out of 62 macrobenthic species reported (Saraladevi, 1986), 11 species were disappeared from the estuarine system during the last two decades (Martin et al., 2011).

Sedimentary Chl-a and Pheo concentrations have not been reported previously from the Cochin estuary. Chl-a concentrations obtained were comparable with those reported in the other estuaries like Orda, Palmones and Baltic sea (Kowalewska et al., 2004; Moreno and Niell, 2004; Szymczak-
Żyla et al., 2011) and lower Chl-α concentrations were observed as compared with Tagus estuary (Cartaxana et al., 2006). Different biotic and abiotic factors affect the spatial and seasonal variations of chlorophyll pigments in the surface sediments (Moreno and Niell, 2004). Chl-α concentrations showed distinct seasonal variations with maximum concentrations in the post monsoon season, minimum in the monsoon season and also displayed a highly significant positive correlation with clay. This is in good agreement with the results of Coljin and Dijkema, 1981 and Moreno and Niell, 2004, who also reported that Chl-α is positively correlated with the clay content and negatively correlated with hydrodynamic energy. Sedimentary pigment concentrations are dependent on the light availability and oxygen content in the water column (Kowalewska and Szymczak, 2004; Kowalewska et al., 2004). The light availability at the sediment surface is affected by the variability in the hydrodynamic conditions (Moreno and Niell, 2004). During the monsoon season daily total solar radiation is less than 350 ly day⁻¹ due to the formation of heavy cloud cover and high rain fall (average 400 mm day⁻¹) (Qasim, 2003). Furthermore, during the monsoon season an increase in the concentration of the suspended particulate matter due to the terrestrial and river run off enhances the water column turbidity leading to a reduction in sufficient light penetration. According to earlier reports (Madhu et al., 2007, 2010), the light attenuation coefficient in the Cochin estuary is higher during the monsoon season when compared to the pre monsoon season (average 2.4±0.4 m⁻¹ and 1.2±0.4 m⁻¹ respectively).

Local water column input of Chl-α is clearly a determinant factor of sedimentary Chl-α concentrations (Szymczak-Zyla and Kowalewska, 2007). The increased water column turbidity and reduction in sufficient light penetration, limit phytoplankton production in water column as
well as in the benthic compartments. A major portion of the primary carbon either settles down or gets transported to the coastal regions during monsoon. High flushing of Cochin backwaters also facilitates faster removal of primary producers to the coastal regions during monsoon (Jyothibabu et al., 2006). Chl-\(a\)/Pheo (Table 4.4) ratios remained below 1 throughout the study period indicating the preponderance of detritus material in the surface sediments. The algal contribution to BPC (Table 4.4) displayed very low values in the study area which ranged from 0.31 to 5.46\% in monsoon, 2.32 to 14.61\% in post monsoon and 1.38 to 8.98\% in pre monsoon season.

<table>
<thead>
<tr>
<th>Table 4.4 Chl-(a)/ Pheo ratios and the percentage of algal contribution to BPC pool in the surface sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorophyll-a/Pheophytin (Chl-(a)/Pheo)</strong></td>
</tr>
<tr>
<td><strong>Stations</strong></td>
</tr>
<tr>
<td>S1</td>
</tr>
<tr>
<td>S2</td>
</tr>
<tr>
<td>S3</td>
</tr>
<tr>
<td>S4</td>
</tr>
<tr>
<td>S5</td>
</tr>
<tr>
<td>S6</td>
</tr>
<tr>
<td>S7</td>
</tr>
<tr>
<td>S8</td>
</tr>
<tr>
<td>S9</td>
</tr>
<tr>
<td>S10</td>
</tr>
<tr>
<td>S11</td>
</tr>
<tr>
<td>S12</td>
</tr>
<tr>
<td>S13</td>
</tr>
<tr>
<td>S14</td>
</tr>
</tbody>
</table>

**4.6.2 Principal Component Analysis**

The quantity and quality of sedimentary organic matter in aquatic systems are mainly controlled by the biogeochemical processes and Principal
Component Analysis (PCA) was employed to deduce it. The parameters for the PCA were selected in such a way that the component of the analysis can give an indication to the significance of biogeochemical processes. The concentrations of individual chemical species will be the net result of these processes and thereby fixing with suitable indicators, it will be possible to identify the relative significance of each process to each species.

In estuarine environment, both geochemical and biochemical processes operate in different magnitude altering the concentrations of nutrients, trace metals and organic matter. The schematic representations of the obtained outputs of PCA are depicted in Fig. 4.5 (a, b & c). PCA analysis for monsoon and post monsoon season derived similar outputs and accounted for a total variance of 83% and 89% respectively. PC1 accounted for a total variance of 61%, exhibited significant loading for texture, TOM, TN and biochemical components which revealed the grain size as the main contribution factor influencing the enrichment of organic matter in surface sediments. This factor revealed the influence of both biochemical and geochemical processes in the surface sediments. It is interesting to note that Chl-a and Pheo concentrations were insignificantly loaded in the first component which implies the substantial contribution of terrestrial derived organic matter in BPC pool. The aforementioned parameters were loaded as a separate component, PC2 which accounts for a total variance of 23%. The fresh algal material is more susceptible to degradation and rapidly utilised by consumers than terrestrial derived organic detritus.

In pre monsoon, the results of PCA generated two PCs which accounts for a total cumulative variance of 79%. The PC1 accounted for a
total variance of 50% with the grouping of clay particles with other biochemical parameters while the PC2 which account for a total variance of 19% revealed the grouping of silt particles with LIP. This clearly indicates the dominance of biochemical processes in pre monsoon season compared to various geochemical processes. PC2 represents geochemical processes such as adsorption and flocculation. LIP being hydrophobic in character adsorbs onto silt and sand particles and ultimately sinks through the water column into the surface sediments. From PCA results it is evident that different geochemical and biochemical processes alter the organic matter concentrations in surface sediments to a greater extent. Both processes alter the nature and quantity of organic matter in estuarine systems. Therefore, a better knowledge on sources of organic matter is essential to identify major biochemical and geochemical processes in estuaries.

![Fig.4.5a Output of PCA for monsoon](image-url)
4.7 Provenance of Sedimentary Organic Matter - Inference from Bulk Organic Matter Techniques

The OC concentrations measured in the sediments of the Cochin estuary during the present study agree well with the ranges reported in previous studies (Balachandran et al., 2005; Martin et al., 2010). OC and
TN concentrations showed highly significant positive correlation with fine grained (silt+clay) sediment and negative correlation with sand content (Table 4.5). Sediment grain size was found to be the main factor influencing the organic matter accumulation in surface sediments of the study region. This is attributed to the close hydraulic equivalence of both organic and mud particles and/or to the relatively high adsorptive capacity of fine particles for organic matter (Cotano and Villate 2006; Ramaswamy et al., 2008).

Table 4.5  Result of correlation analysis of bulk elemental and isotopic ratios with general sediment characteristics.

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>OC</th>
<th>TN</th>
<th>OC/TN</th>
<th>δ(^{13})C</th>
<th>δ(^{15})N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td>-0.88(^{a})</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>-0.86(^{a})</td>
<td>0.52</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OC</td>
<td>-0.83(^{a})</td>
<td>0.77(^{a})</td>
<td>0.67(^{a})</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>-0.88(^{a})</td>
<td>0.77(^{a})</td>
<td>0.77(^{a})</td>
<td>0.94(^{a})</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OC/TN</td>
<td>0.29</td>
<td>-0.18</td>
<td>-0.32</td>
<td>0.01</td>
<td>-0.31</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ(^{13})C</td>
<td>-0.35</td>
<td>0.21</td>
<td>0.41(^{b})</td>
<td>0.51(^{b})</td>
<td>0.46(^{b})</td>
<td>0.12</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>δ(^{15})N</td>
<td>-0.23</td>
<td>0.16</td>
<td>0.25</td>
<td>0.11</td>
<td>0.20</td>
<td>-0.21</td>
<td>0.31</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^{a}\)Correlation is significant at the 0.01 level (2-tailed), \(^{b}\)Correlation is significant at the 0.05 level (2-tailed).

Fig. 4.6 Inter-relationship between OC and TN in surface sediments
The OC and TN exhibited a good linear relationship (Fig. 4.6) in surface sediments of Cochin estuary and the intercept of regression line passes through the origin which indicates very less adsorbed NH$_4^+$ ions in surface sediments. Hence, it is assumed that the measured TN concentrations can be used as a reasonable estimate of organic nitrogen (Liu et al., 2006; Rumolo et al., 2011) and OC/TN used as a better proxy to track the sources of organic matter. The total organic carbon to nitrogen (C/N) ratio has been widely used to differentiate the sources of organic matter in estuaries based on the generalisation that fresh marine autogenic organic matter has C/N ratios between 4 and 9, whereas organic matter derived from terrestrial vascular plants has C/N ratios more than 12 (Meyers 1994; Rumolo et al., 2011). The basic reason for such differences in C/N ratios between vascular plants (>12) and micro algae (5–7) are simply due to the carbohydrate-rich (e.g., cellulose)/ protein-poor and protein-rich/carbohydrate poor nature of each source respectively (Hedges et al., 1986; Orem et al., 1991; Meyers, 1997). The inorganic nitrogen species adsorbed in clay minerals can cause serious errors when applying OC/TN ratios for source characterisation of organic matter in aquatic systems (Meyers, 1994; Schubert and Calvert, 2001; Rumolo et al., 2011). In the present study it was found that the OC/TN ratios displayed high variability in the study region and devoid of any correlation with grain size data.

The OC/TN ratios (Fig. 4.7a) in the surface sediments of Cochin estuary ranged from 12 to 21 (14±3) in monsoon, 11 to 20 (13±3) in post monsoon and 7 to 19 (13±3) in pre monsoon which indicate a mixture of continental derived as well as marine materials in surface sediments. Wu et al., 2002 reported the existence of a negative correlation between the
OC/TN ratios to that of $\delta^{13}$C values. However, the regression analysis revealed that there is no such correlation in the present study (Fig.4.7b). This result is consistent with the previous studies (Liu et al., 2006; Gao et al., 2012) which demonstrated that the decomposition processes such as autolysis, leaching and microbial remineralisation considerably alters the sedimentary OC/TN ratios in surface sediments. The OC/TN was nitrogen ratio of sedimentary organic matter is expected to increase or decrease during sediment diagenesis by the selective degradation of organic matter components (Meyers et al., 1996; Liu et al., 2006). The OC/TN ratios tend to be decrease due to the release of CO$_2$ and CH$_4$ as the degradation products, while it tend to be increase due to the rapid degradation of proteinaceous organic matter than non-nitrogen organic components (Gao et al., 2012). Hence, the organic matter degradation processes may influence the distribution of OC/TN ratios to a great extent.

Fig. 4.7 a) C/N ratios and b) $\delta^{13}$C Vs C/N ratio in surface sediments
Stable carbon isotopic ratios have been widely used for the source characterisation of organic matter in estuaries (Andrews et al., 1998; Liu et al., 2006; Zhang et al., 2009). Terrestrial organic matter produced by C_3 pathway have $\delta^{13}C$ values ranging from -30 to -26‰, while for C_4 pathway, it is from -16 to -9‰ (Pancost and Boot, 2004). Organic matter produced by marine phytoplankton has $\delta^{13}C$ values between -22 and -18‰ (Cifuentes et al., 1998). The $\delta^{13}C$ values of sedimentary organic matter from Cochin estuary were found to be comparable with those obtained from estuaries such as Hunts Bay, Forth estuary, Yangtze estuary and Pearl River estuary (Andrews et al., 1998; Graham et al., 2001; Liu et al., 2006; Zhang et al., 2009). The distributional characteristics of $\delta^{13}C$ values indicate that the organic matter in surface sediments of Cochin estuary is a mixture of terrestrial derived material and marine derived material. The $\delta^{13}C$ values displayed a clear seaward enrichment of heavy carbon isotope which indicates the supply of large amount of marine derived organic matter into the surface sediments towards the seaward side. Several earlier studies demonstrated the seaward increase of $\delta^{13}C$ values (Liu et al., 2006; Hu et al., 2009; Gao et al., 2012) and it is explained as the seaward increase of marine autogenous organic matter relative to the terrigenous organic matter. However, the seaward decrease of $\delta^{15}N$ values and OC/TN ratios were not observed in the present study and the $\delta^{13}C$ values were positively correlated with clay content, OC and TN concentrations, which indicate that the hydrodynamic conditions in the estuary as well as the input of anthropogenic organic matter from the nearby urban areas which influence the $\delta^{13}C$ values to a considerable degree.

Marine organic matter has mean $\delta^{15}N$ values of 5-7‰ derived from phytoplankton which normally use dissolved nitrate (Lamb et al., 2006; Gao et al., 2012). The $\delta^{15}N$ of organic matter derived from nitrogen fixing land
plants is around zero, where as plants using soil nitrogen compounds have usually positive $\delta^{15}N$ values (Gaye–Haake et al., 2005). The anthropogenic organic matter derived from sewage is isotopically rich in heavy nitrogen compounds (Cole et al., 2006). The spatiotemporal distributional features of $\delta^{15}N$ values in surface sediments of Cochin estuary is rather complex. Even though the $\delta^{15}N$ values are in a narrow range of 3.1 to 6.7‰, it did not show any correlation with other physical and chemical parameters in the study region. This may be due to the modification of nitrogen isotopic composition by a wide array of biogeochemical processes. Previous studies have demonstrated that the transformation and recycling of dissolved and particulate nitrogen compounds can cause kinetic isotopic fractionation of nitrogen (Wu et al., 2003; Gao et al., 2012). The organic matter diagenesis tends to increase the $\delta^{15}N$ values in surface sediments (Liu et al., 2006). It is also reported that the nitrogen isotopic enrichment is relative to heterotrophic microorganisms and the $\delta^{15}N$ values of microbial reworked terrestrial organic matter increased from -4 to 9‰ (Caraco et al., 1998). The observed trends in the $\delta^{15}N$ values indicate that the sediment decomposition processes have considerable effects on nitrogen isotopic composition in the Cochin estuary also.

Some marine phytoplankton like *Trichodesmium* fix dissolved molecular nitrogen and $\delta^{15}N$ values of organic matter derived from them is close to zero (Altabet, 1996; Ramaswamy et al., 2008). During the present study, comparatively low $\delta^{15}N$ values were observed in pre monsoon season. This may be due to the occurrence of *Trichodesmium* in the estuary. Many authors reported the occurrence of *Trichodesmium* in the lower reaches of Cochin estuary in pre monsoon period (Gopinathan et al., 1974; Verma and Agarwal, 2000). Joseph, 2005 identified a total number of 75 cyanobacterial species in the Cochin estuary and reported a high density of
these species during the pre monsoon months. The incidence of *Trichodesmium* bloom had frequently been reported form the adjacent coastal waters (Krishnan et al., 2007; Ashadevi et al., 2010).

The potential sources of organic matter in the estuarine sediments are terrestrial detritus, in situ primary production, marine materials and sewage. It was found that the $\delta^{13}$C values were insignificantly correlated with sedimentary Chl-a concentrations (Fig. 4.8). It has been reported in the literature that sewage has no significant impact on the carbon and nitrogen isotopes in estuaries having strong self purification capacities (Liu et al., 2006). Cochin estuary is a dynamic positive estuary having a sporadic introduction of terrestrial organic matter; a large amount of terrestrial organic matter is transported from the catchment of six rivers to the estuary (Thottathil et al., 2008).

![Fig.4.8 Inter-relationship between $\delta^{13}$C and Chl-a content in surface sediments](image)

Hence we disregarded the influence of sewage while calculating the relative proportion of terrigenous input. Furthermore, the $\delta^{15}$N values reflected an
insignificant input of sewage to the sediments only. All these converge to the assumption that organic matter derived mainly from the terrigenous and marine inputs in the surface sediments of the Cochin estuary.

The fraction of terrestrial derived organic matter in surface sediment could be quantitatively estimated using $\delta^{13}C$ based two end member mixing model proposed by Schultze and Calder, 1976. Although the bulk indices such as elemental stoichiometry and bulk isotopic composition have been widely adopted to characterise the sources of organic matter, there have been only limited studies in Indian estuaries. Therefore we are unable to compare our results with any other Indian estuaries and hence we assigned the marine and terrestrial end member values as -30‰ and -20.5‰ respectively considering those reported in previous literatures especially in Chinese estuaries (Wu et al., 2002; Jia and Peng, 2003; Liu et al., 2006; Zhang et al., 2009).

The relative contribution of terrestrial organic matter (F) was calculated using the following equation:

$$F (%) = \left\{ \frac{(\delta^{13}C_{\text{marine}} - \delta^{13}C_{\text{measured}})}{(\delta^{13}C_{\text{marine}} - \delta^{13}C_{\text{terrestrial}})} \right\} \times 100$$

The contribution of terrestrial derived organic matter in surface sediments of Cochin estuary ranged from 13 to 74% (Fig. 4.9) in surface sediments. The terrestrial derived organic matter did not display any seasonal difference, but possess significant spatial variations and showed a decreasing trend from the inner part of the estuary to the seaward side.
4.8 Conclusions

The results of organic carbon content and biochemical components in the surface sediments of Cochin estuary showed comparable concentrations to those reported in highly industrialised and urbanised eutrophic estuaries. Biopolymeric carbon chains were dominated by carbohydrates, followed by proteins and lipids, pointing a nitrogen limitation for heterotrophic metabolism. The input of organic matter from rivers coupled with the discharge of organic wastes from different industrial, agricultural and aquaculture sectors leads to a large scale accumulation of organic matter in the estuarine sediments. The predominance of carbohydrates over sedimentary protein indicates faster mineralisation of proteinaceous organic matter in surface sediments and the estuary behaves as a detrital trap for the accumulation of aged organic matter. Low Chl-$a$ concentrations were displayed during the monsoon when compared to other seasons were due to higher water column turbidity, heavy cloud cover and high rainfall events that limit the light availability for primary
production. The threshold levels of PRT, BPC and algal contribution to BPC suggests the hypertrophic conditions prevailing in and around Cochin harbour region and eutrophic conditions towards the inner part of the estuary.

OC, TN, OC/TN ratios and $\delta^{13}$C in surface sediments of Cochin estuary showed distinct spatial variations, while $\delta^{15}$N did not display any spatial variations in the study region. OC and TN concentrations strongly depend on the granulometric composition of surface sediments in the study region. The $\delta^{13}$C values ranged from -27.5 to -21.7‰ in surface sediments and a gradient was observed towards the seaward side. The $\delta^{15}$N values were found to be more complex in surface sediments and ranged from 3.1 to 6.7‰. The fraction of terrestrial organic matter in total organic matter pool is estimated by $\delta^{13}$C based two end member mixing model and it ranged from 13 to 74% in surface sediments. The distribution features of terrestrial organic matter exhibited significant spatial differences with higher contribution in the inner part of the estuary.

The application of biochemical descriptors and bulk indices like elemental composition and isotopic ratios are useful techniques for the assessment of total quality, benthic trophic status and relative contribution of marine and terrestrial derived organic matter in surface sediments; but the source, fate and degradation pathway of organic matter in the Cochin estuary can be deduced only by a molecular biomarker approach.
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