ABSTRACT:
Eutrophication has often been one of the major problems encountered in estuaries and coastal waters. The oxic/anoxic status of an estuary can be effectively determined by measurement of the sediment oxygen demand (SOD). The present study forms a pioneering attempt to evaluate the SOD of the Cochin Backwater System (CBS), a tropical eutrophic estuary in the south-west coast of India. The CBS exhibited significant spatio-temporal variations in SOD. The mean net SOD during the dry season (2569.73 µmolO₂m⁻²h⁻¹) was almost twice that of the wet season (1431.28 µmolO₂m⁻²h⁻¹), presumably due to higher discharge during the latter season. The observed pockets of net oxygen release indicate that the CBS still retains certain autotrophic regions in spite of heavy organic drains. The low oxygen flux in light chambers points towards the role of microphytobenthos in maintaining the oxygen reservoir of the estuarine system.

Key words: Sediment oxygen demand; dissolved oxygen; estuaries; Cochin backwaters; benthos; microcosm; eutrophication
1. Introduction

The Cochin Backwater System (CBS), a tropical monsoon impacted estuary, is the second largest estuarine system in India. It is fed by six rivers (Achenkovil, Pampa, Manimala, Meenachil and Muvattupuzha in the south and a branch of the Periyar in the north) discharging about $2 \times 10^{10} \text{m}^3\text{y}^{-1}$ of fresh water (Srinivas, 2000; Srinivas et al. 2003a, 2003b). CBS (256 km$^2$), with a volume of 0.55 km$^3$ (Gopalan et al. 1983), is regarded as part of the Vembanad-Kol, one of the largest wetlands along the west coast of India. Being a micro tidal estuary (<1m), the CBS undergoes a characteristic transformation from a river dominated system during the wet season (June-September) to a tide-dominated system during the dry (February-May). The rich nutrients received through freshwater influx makes CBS highly productive during the wet season (Madhu et al. 2007). Similarly, the tidal activity transforms the estuary into a vertically mixed, eutrophic system with high organic production during the dry season.

CBS, a net positive autotrophic system, has recently been reported to have shifted towards heterotrophy (Shoji et al. 2008; Gupta et al. 2009). This shift in productivity pattern was presumed to be the outcome of allochthonous organic inputs by rivers. Moreover, the CBS receives large amount of untreated industrial ($10^4 \times 10^3 \text{m}^3$) and domestic (0.26 x10$^3$ m$^3$) effluents from Kochi and its satellite towns (KSPCB 1982, 1986; Balachandran et al. 2006). The increased bacterial heterotrophic activity due to enhanced nutrient levels has resulted in CO$_2$ supersaturation and subsequent oxygen undersaturation (Garnier et al. 1999; Gupta et al. 2009). That is, the oxygen used up for bacterial degradation of organic matter (heterotrophy) is much greater than that generated by primary productivity (autotrophy).

In view of the heterotrophic nature of CBS (Gupta et al. 2009), it is vital to scrutinize the Sediment Oxygen Demand (SOD) of the organically enriched sediments. The SOD can be best defined as the rate of oxygen consumption owing to the respiration of the benthic biotic communities and the coexisting biochemical degradation of organic matter. This implies that higher the organic load, greater the oxygen utilised for its mineralisation. Hence, the present study was undertaken to elucidate the SOD in CBS.

2. Materials and Methods

2.1. Benthic Microcosm experiment

There are generally two categories of techniques for measuring SOD; laboratory measurement of sediment core samples and in situ field measurement using submersible benthic chambers. Both methods have their own pros and cons. However, transportation of sediment from the site to the laboratory inevitably involves a certain degree of disturbance to it, no matter how careful the process is. The extent of reproducibility of ambient field conditions in the laboratory may also affect the accuracy of the measurements. The delayed measurement of sediment samples may also have a negative impact. In situ field measurements can minimize manipulation of sediment and can reflect ambient field conditions well. The method of in situ benthic flux chambers has been prevalently used for determination of fluxes across the sediment–water interface. Flux calculations by the use of benthic flux chambers have the advantage of integrating fluxes over a large surface of sediments, thus minimizing variations due to small-scale sediment heterogeneity (Tessier et al. 1994). Therefore, during the present study, SOD was determined using benthic microcosm experiments, wherein, the oxygen flux across the sediment-water interface was measured by means of in situ stirred light and dark chambers (Hammond et
These cylindrical chambers (radius, 0.15 m and height, 0.2 m) enclose a water column of 14.13 litres and the base of each chamber covers an area of 0.71 m². They are constructed of transparent plexiglass which can transmit ~ 92% of the photosynthetically active radiation (PAR). The chambers, secured to metal frames, were deployed on the seabed by SCUBA divers in such a way that the lower 5 cm penetrates into the sediment. The stirring device inside the chamber was driven by a motor with a variable speed of rotation (mini-motor) in order to stimulate a current speed approximating that found in the proximity of the sediment and thus to get a homogenous water mass within the chamber. The delicate stirring was performed for 20 minutes at an interval of 15 minutes using a timer. Power was transmitted from the motor (driven by 12-volt rechargeable battery) to the stirring device by magnetic induction coupling.

Position for Figure 1

The benthic microcosm experiments were conducted during the dry (April 2010) and wet (August 2010) seasons at six sampling locations in the CBS (Fig.2). Chambers were deployed based on tidal rhythm (Highest High Tide-HHT, High Tide-HT, Low Tide-LT and Lowest Low Tide-LLT). After deployment, the chambers were incubated for a period of three hours prior to sampling. Water samples enclosed within the chamber were collected through silicon tubing using a peristaltic pump positioned onboard the anchored boat. A one-way valve was secured to one side of each of the chambers for replacement-water to flow in during sampling. The dilution produced within the chamber by the sampling was less than 3% of the total volume of the chambers. The equipment could withstand hydrostatic pressure down to a depth of 20 m.

Position for Figure 2

2.2. Oxygen Flux

Benthic O₂ Flux was calculated using the formula:

$$FLUX = \frac{(C_i - C_f) \times V}{H \times A}$$

where; FLUX = benthic O₂ flux in μmol·m⁻²·hr⁻¹, $C_i$ = initial concentration, $C_f$ = final concentration; $V$ = volume of water enclosed in the benthic chamber; $H$ = incubation time in hours and $A$ = area under the benthic chamber. The oxygen flux in the dark chamber corresponds to sediment oxygen demand, SOD (oxygen required to satiate respiration of benthic organisms, chemical reactions and bacteria-mediated redox reactions at the sediment-water interface) while the flux in light chamber corresponds to net oxygen variation (i.e., oxygen production-SOD).

2.3. Hydrographic Parameters

Samples were collected for the analysis of water quality parameters such as temperature, salinity, pH and DO with a 5L Niskin water sampler and were measured onboard using a multiparameter probe (Eutech Instruments).
The data quality of the temperature, salinity and pH values were confirmed in comparison with the CTD (Sea-Bird Electronics) measurements and that of DO using the conventional Winkler’s method (Grasshoff et al. 1983).

2.4. Sediment Analysis

Sediment samples were collected using a Van-Veen grab (0.048 m²) for analyzing the texture, organic matter, microphytobenthos (MPB) and macrobenthos. The texture of the sediment was analysed using Particle Size Analyser (Sympatec). Sediment organic carbon was estimated by the procedure of El Wakeel and Riley modified by Gaudette and Flight (1974). The amount of organic matter was obtained by multiplying the organic carbon values with 1.724 (Nelson and Sommers, 1996). MPB biomass was estimated using acetone extraction (Lukatelich and McComb, 1986; Ouisse et al. 2011). 10ml of 90% acetone was added to the sediment. The sediment suspension was left to extract in the dark for 4 h at 4°C. A subsample (~ 8 ml) was removed and centrifuged for 8 min at 3500 rpm to settle any particulate material. Chlorophyll a and phaeophytin concentrations were estimated using spectrophotometer and expressed as mg Chl a m⁻².

For the analysis of numerical abundance of macrobenthos, samples were sieved through a 500µ mesh screen (Birkett and McIntyre, 1971) and preserved in 10% buffered formalin with Rose Bengal stain and thereafter, counted under an illuminated magnifier (OPTO MAG 9).

2.5. Statistical Analysis

The significant differences between hydrographic parameters from different stations were determined by one-way ANOVA and multiple comparison tests (Fischer’s Least Significant Difference). The inter-relationships between the various parameters and SOD were analysed using correlation analysis (SPSS version 16).

3. RESULTS

3.1. Hydrographic Parameters

The south-west monsoon significantly influenced the hydrography of CBS. Salinity varied widely between the dry and wet periods, with the lowest being recorded at Varapuzha (dry season, 0.05; wet season, 0.03‰) and highest at Maliankara (dry season, 30.32 ‰; wet season, 18.26 ‰, Fig.3). During dry season, the estuarine water column was relatively warm (30.08-32.85 ° C) compared to the wet seas on (28.03-29.93° C, Fig.3). The pH ranged from 6.7 to 7.84 during the dry season, while it remained almost steady during the wet season throughout the estuary (av. 6.78). The dissolved oxygen (DO) content in the water column ranged from 3.56 to 5.42 µg ml⁻¹ during dry season and from 3.82 to 5.56 µg ml⁻¹ during wet season. All the hydrographic parameters exhibited significant differences between the stations during dry and wet seasons (p<0.05), except for pH during wet season (p=0.448).

Position for Figure 3

3.2. Physical and chemical characteristics of the sediment

The textural analysis indicated a predominance of sandy fraction at Maliankara and Fort Kochi during both the seasons, while at Nedungad there was a shift from sandy-silt in dry season to silty-sand during wet season. At Varapuzha and
Arookutty, the sediment changed in texture from clayey-silt in dry season to sandy-silt during wet season, while at Thanneermukkam it was silty-sand during both the seasons (Fig.4). The sediment organic matter exhibited an increasing trend from northern to central estuary, followed by a sharp decline at Arookutty and relative upsurge at Thanneermukkam during both the seasons (Fig.5).

Position for Figure 4

Position for Figure 5

3.3. Microphytobenthos (MPB)

Significant decrease in MPB biomass (expressed as chlorophyll $a$ concentration) was observed during wet season, compared to the dry season in the northern and central estuary. The highest biomass was observed at Varapuzha (dry season, 76.22 mg m$^{-2}$; wet season, 37.31 mg m$^{-2}$), followed by Fort Kochi (dry season, 38.47 mg m$^{-2}$; wet season, 18.64 mg m$^{-2}$) during both the seasons, while Maliankara (dry season, 18.62 mg m$^{-2}$; wet season, 8.27 mg m$^{-2}$) and Thanneermukkam (dry season, 8.74 mg m$^{-2}$; wet season, 11.42 mg m$^{-2}$) recorded the lowest values (Fig.6). Phaeopigment to chl $a$ ratios were <0.5 throughout the estuary during both the seasons, except for Thanneermukkam during dry season.

Position for Figure 6

3.4. Numerical abundance of macrobenthic fauna

The total macrofaunal abundance varied between 271 (Varapuzha) and 3166 No/m$^2$ (Arookutty) in the dry season and between 42 (Varapuzha) and 2854 No m$^{-2}$ (Arookutty) in the wet season (Table 1). All the stations were dominated by annelids, followed by arthropods during both the seasons.

Position for Table 1

3.5. Sediment Oxygen Demand (SOD)

SOD, i.e., the oxygen flux in dark chamber, in CBS ranged from 1829.48 µmol m$^{-2}$ h$^{-1}$ (Maliankara) to 4420.81 µmol m$^{-2}$ h$^{-1}$ (Thanneermukkam) in dry season and from 342.06 µmol m$^{-2}$ h$^{-1}$ (Varapuzha) to 2549.87 µmol m$^{-2}$ h$^{-1}$ (Maliankara) in wet season. During dry season, SOD in all the stations varied significantly ($p$=0.01). Least Significant Difference (LSD) analysis showed that the mean SOD value was significantly different for Thanneermukkam compared to the other stations ($p$<0.05). During wet season also, the SOD in the different stations varied significantly ($p$<0.05). LSD analysis showed that the mean SOD varied significantly for Varapuzha ($p$<0.05). The oxygen flux observed in light chambers was generally low compared to the dark chambers, with the major exception being Varapuzha during both the seasons (Table 2). The study revealed the presence of pronounced spatio-temporal variations in SOD of the CBS. The mean net SOD during the dry season (2569.73 µmol m$^{-2}$ h$^{-1}$) was almost twice that of the wet season (1431.28 µmol m$^{-2}$ h$^{-1}$). Another interesting observation is the reversal of SOD between northern and southern regions of CBS during the two seasons. During dry season, the southern region of the estuary (Thanneermukkam) exhibited much higher SOD than the northern region (Maliankara). Unlike this, during wet season, the northern region of the estuary had a higher SOD than the
southern region, with an exceptionally low SOD (342.06 µmol m\(^{-2}\) h\(^{-1}\)) being observed at Varapuzha. In fact, Varapuzha exhibited much higher oxygen flux in light chamber compared to dark chamber, irrespective of the seasons (dry season, 4497.37 and wet season, 1674 µmol m\(^{-2}\) h\(^{-1}\)). Tidal rhythms do not seem to have any consistent effect on SOD at the various stations.

Position for Table 2

4. DISCUSSION

Coastal environments that exhibit deficiencies in water column dissolved oxygen (DO) are becoming increasingly prevalent due to increasing anthropogenic nutrient loading and the subsequent eutrophication of the water system (Nixon, 1995; Diaz and Rosenberg, 1995; Cloern, 2001; Gray et al. 2002). The proliferation of hypoxic and anoxic (i.e., no measurable DO) areas along inhabited coastlines is considered as one of the most critical environmental problems menacing marine ecosystems in modern times (GESAMP, 2001; USCOP, 2004). Conventionally, the Biochemical Oxygen Demand (BOD) in the water column is used as an indicator of the organic quality of water bodies. However, for obtaining a more realistic picture of the oxygen demand, Sediment Oxygen Demand (SOD) in the system also should be taken into consideration. In fact, SOD and BOD are equally important in determining the oxic/anoxic status of the estuarine ecosystem. Considering the fact that the CBS receives large amount of untreated industrial and domestic wastes per day (Martin et al. 2011), SOD might prove to be an additional tool in assessing its environmental quality. In this regard, the present study forms a pioneering attempt to evaluate the SOD of the CBS.

The observed spatio-temporal variations in SOD can primarily be attributed to changes in various physico-chemical and biological parameters like salinity, organic load, microphytobenthic biomass, macrofaunal abundance etc., which either independently or collectively, affects the SOD. For example, the very high SOD observed in the southern region, especially in Thanneermukkam (4420.81 µmol m\(^{-2}\) h\(^{-1}\)), during dry season is probably due to the observed high organic load. High load of organic matter depletes DO from the water column in proximity to the sediment through enhanced bacterial respiration and biochemical reaction, thereby, leading to substantial increase in SOD (Chau, 2002). In addition to this, the relatively low chlorophyll \(a\) concentration (8.74mg/m\(^2\)) together with > 0.5 phaeophytin:chlorophyll \(a\) ratio (0.59) points towards the presence of a stressed MPB population at this station (Shuman and Lorenzen, 1975; Bidigare et al. 1986; Sanilkumar et al. 2009). The drop in SOD in the southern region during wet season can directly be linked to the substantial decrease in salinity and organic load. The enhanced dissolution of atmospheric oxygen in the overlying water column due to low saline conditions during wet season might have led to a reduction in the oxygen demand (Singbal, 1976; Qasim and Sen Gupta, 1981; De souza and Sen Gupta, 1986). Further, the low organic load might have reduced the oxygen requirement for its mineralization. The higher SOD in the northern region of the estuary compared to southern region during wet season can be attributed to the higher organic load. In earlier studies also, SOD is found to be highly correlated with organic matter concentration (Ling et al. 2009).

The freshwater dominated zone of the estuary, Varapuzha, was the only station showing a higher oxygen flux in light chamber compared to dark chamber, in spite of heavy organic drains by the rivers. This can be attributed to the greater MPB presence as evidenced from very high chlorophyll \(a\) and very low phaeophytin: chlorophyll \(a\) ratio (dry season, 0.16 and wet season, 0.49). That is, the photosynthetic activity of MPB enclosed by the light chambers is responsible for
the increased oxygen production. Also, this station had the least macrobenthic abundance during both the seasons (Table 1).

In comparison with previous reports pertaining to SOD in other shallow water ecosystems (Table 3), the oxygen demand in CBS (1.97 and 0.77 gO$_2$ m$^{-2}$ day$^{-1}$ in the dry and wet seasons, respectively) seems to be relatively low. Worldwide, the highest SOD observed so far (33 gO$_2$ m$^{-2}$ day$^{-1}$) has been in the eastern US rivers, followed by Semariang Batu River, Malaysia (21.4 gO$_2$ m$^{-2}$ day$^{-1}$; Bowie et al. 1985; Ling et al. 2009). While the high SOD in eastern US rivers was mostly due to high organic matter input from river discharge, the study site in Semariang Batu River recorded high values as a consequence of effluent discharge from shrimp farms, residential areas and boat jetty. In the study conducted at Semariang Batu River, Malaysia, significantly low SOD was observed for stations with no human interference. This emphasizes the fact that anthropogenic activities are the primary contributors to increase in SOD.

Position for Table 3

The CBS also has similar environmental and allochthonous inputs as in the above two cases, but the observed SOD is far too low. Although the SOD was high in certain regions, no consistent trend was evident throughout the estuary. Moreover, there are pockets of net oxygen release as observed in Varapuzha. The rich MPB biomass probably acts as one of the major contributors to the oxygen reservoir of the estuary, as evidenced by the high SOD in dark chambers, especially at Varapuzha. The observed higher incidence of SOD during dry season compared to wet season is probably because high river discharge resulted in higher flush and short residence time. Thus, it can be inferred that in spite of the heavy organic drains, the CBS still retains certain pockets of net autotrophy. However, detailed investigations on SOD of CBS is necessary to ascertain the trophic status and thereby, the health of this important estuarine system.

Acknowledgements

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Table 1. Numerical abundance of macrobenthos in the study area

<table>
<thead>
<tr>
<th>Station</th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maliankara</td>
<td>2166</td>
<td>542</td>
</tr>
<tr>
<td>Nedungad</td>
<td>979</td>
<td>1542</td>
</tr>
<tr>
<td>Varapuzha</td>
<td>271</td>
<td>42</td>
</tr>
<tr>
<td>Fort Kochi</td>
<td>1063</td>
<td>2270</td>
</tr>
<tr>
<td>Arookutty</td>
<td>3166</td>
<td>2854</td>
</tr>
<tr>
<td>Thanneermukkam</td>
<td>1105</td>
<td>146</td>
</tr>
</tbody>
</table>

Table 2. Oxygen flux in the benthic chambers deployed in the CBS during dry and wet seasons, LC (Light Chamber) and DC (Dark Chamber)

<table>
<thead>
<tr>
<th>STATION</th>
<th>DRY SEASON</th>
<th>WET SEASON</th>
</tr>
</thead>
<tbody>
<tr>
<td>STATION</td>
<td>LC</td>
<td>DC</td>
</tr>
<tr>
<td>Maliankara</td>
<td>1083.18</td>
<td>1829.48</td>
</tr>
<tr>
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<td>1601.44</td>
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<tr>
<td>Varapuzha</td>
<td>4497.37</td>
<td>2150.80</td>
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<td>Fort Kochi</td>
<td>580.46</td>
<td>2321.83</td>
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<tr>
<td>Arookutty</td>
<td>2295.92</td>
<td>2404.75</td>
</tr>
<tr>
<td>Thanneermukkam</td>
<td>3824.8</td>
<td>4420.81</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>2313.86</strong></td>
<td><strong>2569.73</strong></td>
</tr>
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</table>
Table 3. Comparison of SOD in CBS with that of other shallow water ecosystems

<table>
<thead>
<tr>
<th>Location</th>
<th>SOD (gO₂/m²/day)</th>
<th>Reference</th>
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<tr>
<td>Upper Illinois waterway</td>
<td>0.56–6.00</td>
<td>Butts, 1974</td>
</tr>
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<td>Northern Illinois rivers</td>
<td>0.27–9.8</td>
<td>Bowie et al. 1985</td>
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<tr>
<td>Eastern US rivers</td>
<td>0.1–33.0</td>
<td>Bowie et al. 1985</td>
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<td>New Jersey rivers</td>
<td>1.1–12.8</td>
<td>Bowie et al. 1985</td>
</tr>
<tr>
<td>Upper Wisconsin river</td>
<td>0.022–0.92</td>
<td>Bowie et al. 1985</td>
</tr>
<tr>
<td>Taiwan’s Keelung River</td>
<td>0.24–1.58</td>
<td>Bowie et al. 1985</td>
</tr>
<tr>
<td>Eastern Michigan rivers</td>
<td>0.10–5.3</td>
<td>Bowie et al. 1985</td>
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<td>Chesapeake Bay</td>
<td>1.6–3.1</td>
<td>Boynton and Kemp, 1985</td>
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<tr>
<td>Lake Ton-Ton (Uruguay)</td>
<td>0.9–1.74</td>
<td>Sommaruga, 1991</td>
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<td>Shing-Mun River, Hong Kong</td>
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<td>Missouri</td>
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<td>Borsuk et al. 2001</td>
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<td>Upper Klamath and Agency Lake, Oregon</td>
<td>1.60</td>
<td>Wood, 2001</td>
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<td>Tolo Harbor, Hong Kong</td>
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<td>Matlock et al. 2003</td>
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<td>Balcom et al. 2007</td>
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<td>Georgia’s coastal plain</td>
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<td>Utley et al. 2008</td>
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<td>Semariang Batu River, Malaysia</td>
<td>0.76–21.4</td>
<td>Ling et al. 2009</td>
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<tr>
<td>Keelung River, Taiwan</td>
<td>0.24–1.58</td>
<td>Liu, 2009</td>
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<td><strong>Cochin Backwater System</strong></td>
<td><strong>0.77–1.97</strong></td>
<td><strong>Present study</strong></td>
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Figure Captions:

**Fig.1.** Benthic microcosm experiment in the Cochin Backwater System

**Fig.2.** Sampling locations in the Cochin Backwater System

**Fig.3.** Salinity, temperature, pH and DO profiles in the CBS during dry and wet seasons (Mal, Maliankara; Ned, Nedungad; Var, Varapuzha; Fort, Fort Kochi; Aroo, Arookutty; Thann, Thanneermukkam)

**Fig.4.** Textural characteristics of the sediment in the CBS during dry and wet seasons

**Fig.5.** Organic load in the CBS during dry and wet seasons

**Fig.6.** Chlorophyll $a$ and phaeophytin levels in the CBS during dry and wet seasons
Fig. 1.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.