Fate and source distribution of organic constituents in a river-dominated tropical estuary

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We investigated spatial and temporal changes in the quality of sedimentary organic matter and trophic status of the Cochin estuarine system, southwest coast of India. Sediment samples were collected in five sampling campaigns from January 2009 to April 2010. TOC/N ratio implied mixed input of autochthonous as well as remarkable allochthonous terrestrial higher plant debris into the sedimentary system. More depleted $\delta^{13}\text{C}$ values at riverine and industrial zone suggested a major contribution of terrestrial higher plant debris to sedimentary organic matter. Trophic status of the estuary changed seasonally to eutrophic via oligotrophic and mesotrophic conditions during the period January 2009 to April 2010. The protein to carbohydrate ratio was lower (<1), indicating heterotrophic nature and the higher lipid to carbohydrate ratio (>1) denoted preservation of lipid compounds in the sediments. Correlation analyses provide evidence of the association of chlorophyll pigments with carbohydrates and account for the highly productive nature of the estuary and algal contributions to organic matter. Canonical correspondence analysis clearly illustrated prominence of phaeopigments in fishing zone, lipids in sewage/tourism influenced zone, carbohydrates in riverine zone and proteins in industrial zone. It also indicated the influence of sedimentary texture, pH and organic carbon to the distribution of biochemical constituents.

1. Introduction

Source characterization of organic matter (OM) within the estuarine sediments is of utmost importance in understanding the autochthonous and allochthonous input as well as to assess global biogeochemical cycles (Yamamuro 2000; Goni *et al.* 2003). *In situ* biological production and accumulation of marine and terrestrial particles have been recognized as the significant sources of OM implies to the estuarine sediments (Mayer *et al.* 1988; Cifuentes 1991). Urban sewage inputs strongly influence the quantity and quality of incoming materials in the sediments and therefore the nature of organic materials depend on complex

physicochemical processes occurring in overlying water layers and in the sediments (Cotano and Villate 2006). Bulk geochemical parameters are available for the evaluation of OM sources and its fate within marine sediments, including biochemical composition, elemental and stable isotope ratios. Biochemical composition serves not only as a valid methodology to determine the origin of organic matter (Colombo *et al.* 1996), but also as a useful tool to evaluate the nutritional quality of organic materials as available food for benthic consumer organisms (Dell'Anno *et al.* 2000; Rossi *et al.* 2001; Rossi and Lardicci 2002; Cividanis *et al.* 2002; Joseph *et al.* 2008). Composition of OM in sediments has been recognized as the major

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factor affecting metabolism, distribution and dynamics of benthic organisms (Grant and Hargrave 1987; Graf 1989; Duineveld *et al.* 1997) and has been widely employed to evaluate the trophic state of both marine and estuarine ecosystems (Cloern 2001; Renjith *et al.* 2012; Akhil *et al.* 2013). The portion of sedimentary OM which are more readily available to benthic consumers (labile fraction), has usually been assessed by estimation of the main biochemical classes of organic compounds (Fichez 1991; Danovaro *et al.* 1993; Fabiano *et al.* 1995; Dell'Anno *et al.* 2002).

Cochin estuary is a highly productive ecosystem, and its complex nature is attributed to permanent connection with the Arabian Sea and the input of significant quantities of OM and nutrients (Srinivas 2000). Large quantities of sewage and other untreated and partially-treated pollutants have been discharged into the estuary, which causes significant toxic impact on the aquatic environment (Balachandran *et al.* 2005, 2008). Even though the estuary has been found to be a site of positive net ecosystem production (Qasim 2003), a seasonal shift in net pelagic production to heterotrophic conditions owing to terrestrial input of OM has also been reported (Thottathil *et al.* 2008). Even though, information regarding the organic geochemical aspects of sediments in the Cochin estuarine system is available (Aneeshkumar and Sujatha 2012; Gireeshkumar *et al.* 2012; Renjith *et al.* 2012; Akhil *et al.* 2013), a long term monitoring and detailed description of the sedimentary variables is yet to be attempted. All these investigations have repeatedly demonstrated the role of industrialisation, urbanisation and other anthropogenic interventions, creating alterations in the biogeochemical aspects and ecological functioning of this sensitive ecosystem. Repeated regular assessment coupled with seasonal changes is a prerequisite for evaluating the current health status of a deteriorating and vulnerable ecosystem. All these factors prompted us to carry out a long term investigation to identify the nature and origin of organic matter and its distribution pattern in the estuary. The study aims at:

- (i) a comparative evaluation of spatio-temporal variability in biochemical components and the processes governing their distribution,
- (ii) to assess the quantity and quality of sedimentary organic matter, and
- (iii) identify the distribution pattern and source characterization of sedimentary organic matter in the Cochin estuarine system using bulk parameters.

The information furnished in the present investigations will be helpful to future researchers as

reference data for formulating remedial environmental conservation strategies.

2. Data and methods

The Cochin estuarine system – CES (latitude: 9°40' and 10°12'N and longitude: 76°10' and 76°30'E) forms a complex network of shallow brackish water (250 km²) running parallel to the coast, and has been designated as a 'Ramsar site' (No. 1214, figure 1). This tropical aquatic system is under the profound influence of the southwest monsoon (Jayaprakash 2002), accordingly three seasonal conditions prevailing, viz., monsoon (June–September), post-monsoon (October–January) and pre-monsoon (February–May). Six rivers (namely: Periyar, Muvattupuzha, Pamba, Manimala, Meenachil and Achencovil) discharge about 20,000×10⁶ m³ of fresh water into the estuary annually (Srinivas 2000). Hydrobiological studies (Menon *et al.* 2000) reflected high flushing taking place in the water body during the monsoon. The variation in the river discharge and heavy rain fall induces a salinity gradient, which is responsible for the diverse biotopes of plankton communities in the estuary (Dayala *et al.* 2014). The northwestern part frequently develops flow restrictions due to converging tides entering from two adjacent inlets, whereas the southern arm experiences tidal amplification (Balachandran *et al.* 2008). This well-known biodiverse wetland is under the threat of severe ecological degradation due to massive reclamation (Gopalan *et al.* 1983) and increased industrialisation and urbanisation (Menon *et al.* 2000; Qasim 2003). In this context, the surface sediment samples were collected from fifteen selected sites (figure 1). Karippadam (S1), Murinjapuzha–Enadhi (S2), Murinjapuzha–Bhramamangalam (S3) and Murinjapuzha (S4) were categorised as riverine zone, while, Perumbalam (S5), Aroor (S6) and Thevara (S7) were referred as fishing zone. The central part of the study area includes: Marine Sciences Jetty (S8), Bolgatty (S9) and Mulavukad (S10), were classified as sewage/tourism influenced zone. While the stations, Chennoor (S11), Cheranellur (S12), Eloor (S13), Edayar (S14) and Kalamassery (S15) together constituted the industrial zone.

Surface sediment samples (5 cm) were collected from the selected stations along the Cochin estuary by a van Veen grab (0.042 m²) in five sampling campaigns, viz., January 2009 (post-monsoon; POM09), April 2009 (pre-monsoon; PRM09), August 2009 (monsoon; MON09), January 2010 (post-monsoon; POM10) and April 2010 (pre-monsoon; PRM10). The sediment pH was determined *in situ* using a portable pH meter (Eutech,

Figure 1. Location map of the study area.

pH Tester 10). Redox potential of the wet sediments were measured by portable Eh meter (Eutech, ORP Testr 10), calibrated with Zobell solution. Texture of the sediments was determined by pipette analysis after removing the inorganic carbonates using 10% HCl and the organic matter using H_2O_2 (Folk 1974). Sediments were freeze-dried, homogenised using agate mortar and pestle and were used for the estimation of geochemical variables. Total nitrogen (N) and total sulphur (S) were determined using CHNS analyzer (Vario EL III). Total organic carbon (TOC) was estimated by TOC analyzer (VARIO TOC SELECT-Elementar), after removing inorganic carbon using 2 M HCl.

Analysis of protein (PRT) was carried out by spectrophotometric method (Lowry *et al.* 1951; Rice 1982) using bovine albumin as standard. Total carbohydrates (CHO) were estimated according to Dubois *et al.* (1956) employing glucose as standard. Total lipids (LPD) were extracted according to Bligh and Dyer (1959) and were estimated according to Barnes and Blackstock (1973) utilising cholesterol as calibration standard. Tannin and lignin (TL) in sediments were estimated spectrophotometrically by the sodium tungstate-phosphomolybdic acid method (Nair *et al.* 1989;

APHA 1995). Chlorophyll and phaeopigments (Phe) estimations were carried out according to standard procedures (Lorenzen and Jeffrey 1980; APHA 1995). Pigments were extracted with 90% acetone (24 hr in the dark at 4°C). After centrifugation, the supernatant was used to determine chlorophyll pigments (chl-*a*, chl-*b* and chl-*c*) and was acidified with 0.1 N HCl to estimate the concentration of phaeopigments. Concentrations of protein, carbohydrate and lipid were converted to carbon equivalents by using the following conversion factors: 0.49, 0.40 and 0.75 g of C/g, respectively (Fabiano and Danovaro 1994). The sum of protein, carbohydrate and lipid carbon is referred as biopolymeric carbon (BPC) (Fichez 1991; Fabiano *et al.* 1995). The algal contribution to BPC was calculated as the percentage of chl-*a* to BPC concentrations, after converting chl-*a* concentration into carbon equivalents, by applying a mean value of 40 (Pusceddu *et al.* 2009). Stable carbon isotope analysis of total organic matter was carried out using Flash EA interfaced with Isotope Ratio Mass Spectrometer (FINNIGAN DELTA PLUS XP, Thermo Electron Corporation). Stable carbon isotope abundances were presented as $\delta^{13}\text{C}$ values and were expressed relative to the Pee Dee Belemnite (PDB) standard. Measurement/estimation of

all the variables were carried out in triplicate and the average value/concentration was reported.

Analysis of variance (ANOVA – two-way without replication) was employed to evaluate the spatial and temporal distributions of the parameters in the study region. Pearson correlation (derived using software SPSS 13) and canonical correspondence analysis (XLSTAT version 2014.6.03) were employed to identify the source of organic matter as well as the process governing the distribution of various geochemical variables in sediments.

3. Results and discussion

The grain size has immense influence on the distribution of various sedimentary parameters in the aquatic environments (Prasad and Ramanathan 2008; Wen *et al.* 2008; Renjith *et al.* 2011). Texture analysis showed a progressive increase in fine fractions from riverine zone to the sewage/tourism influenced zone (figure 2). Increased river run-off associated with high precipitation during monsoon (Menon *et al.* 2000) results in higher sand content, more prominently at the industrial zone (S13, MON09). The textural composition of the sediment displayed distinct spatial as well as seasonal variations ($p < 0.01$). Considerable alterations in the texture was observed in the sediments of fishing (S5–S7), sewage/tourism influenced (S8–S10), riverine zone (S1–S4) and industrial zone (S11–S15). Sediments from a majority of stations exhibited significant fluctuations in textural characteristics indicating the discharge dependency in the study area. Fine sediments get entrained during the river run-off, leaving behind the coarser sediments in the river-dominated locations of the study region. Sorting processes like scouring by tides, result in re-suspension and flushing out of sediments (Muraleedharan Nair and Ramachandran 2002). Furthermore, the complex current pattern prevailing in the estuarine area also contributes to the textural inhomogeneity in sediments (Rasheed 1997).

pH of the sediment was mainly controlled by the river run-off as well as ingress of sea water from the Arabian Sea and fluctuated between 6.65 (S12; PRM10) and 8.3 (S8; PRM09). The observed range for redox potential was noted to be from –345 (S9; PRM09) to 21 mV (S2; PRM10), providing clues for degradation of organic matter in sediments. Qualitative evaluation of the redox status of the sedimentary environment was assessed by total organic carbon to sulphur ratios (Raiswell *et al.* 1987). Typically TOC/S ratios >5 has been categorized as oxic sediment with oxygenated bottom water, TOC/S = 1.5–5 indicates sediments deposited under periodic anoxia and

TOC/S <1.5 reflect anoxic sediments with anoxic water (Raiswell *et al.* 1987). The estimated TOC/S values (range: 0.30–9.52) pointed out that most of the stations were under the influence of periodic anoxia, where sediments undergo sulphate reduction below an oxygenated water column (Niffy Benny 2009; Renjith *et al.* 2012; Akhil *et al.* 2013).

Higher concentration of TOC (range: 0.16–6.39%) recorded in fine-grained sediments, seems to display remarkable spatial variation ($p < 0.01$). The distribution pattern of TOC with texture is depicted in figure 2. During the investigation, TOC levels were high in the riverine (S1, S2, S3) and industrial zones (S12, S14, S15), on account of the transport of allochthonous material via terrestrial run-off (Martin *et al.* 2010; Gireeshkumar *et al.* 2012; Renjith *et al.* 2012). Surficial sediments of the CES recorded a moderate level of TOC comparable to previous studies (Balachandran *et al.* 2005; Joseph *et al.* 2008; Martin *et al.* 2010; Deepulal *et al.* 2012; Gireeshkumar *et al.* 2012; Renjith *et al.* 2012; Akhil *et al.* 2013). Organic matter constitutes an integral part of aquatic sediments and its distribution pattern in the study region was noted to be governed by the *in situ* primary production, supply rate of terrestrial materials, deposition rate and texture of the sediments. Textural control over TOC was indicated by the correlation of TOC with sand, silt and clay sediments. TOC exhibited a significant positive correlation with both silt ($r = 0.32$) and clay ($r = 0.25$) and an inverse relationship with that of sand ($r = -0.33$) in the estuarine sediments (table 2). Positive relationship of TOC with clay and silt (figure 2) indicated its size-dependent scavenging (Muraleedharan Nair and Ramachandran 2002). Coatings of organic matter onto clay minerals tend to affect size distribution and settling rates of sediments (Cotano and Villate 2006; Ramaswamy *et al.* 2008).

Seasonal variation in the estimated biochemical components in sediments, followed the trend: LPD $>$ CHO $>$ PRT-POM09, CHO $>$ PRT $>$ LPD-PRM09, CHO $>$ PRT $>$ LPD-MON09, PRT $>$ CHO $>$ LPD-PRM10, PRT $>$ CHO $>$ LPD-POM10. Total carbohydrate in the sediments (table 1) varied from 434.19 to 12839 mg/kg with significant spatial variations ($p < 0.01$). The increased contents of CHO (figure 3) was recorded at riverine (S1) and industrial zone (S12, S14, S15) implying greater contribution of vascular plant debris to sedimentary OM (Cowie and Hedges 1984). Furthermore, the predominant concentration of CHO over PRT and LPD during PRM09 and MON09 (figure 3) indicated the input of allochthonous terrestrially derived OM and the detrital-heterotrophic nature of CES (Danovaro 1996; Renjith *et al.* 2012). The observed levels of CHO were in good agreement

Figure 2. Seasonal and spatial variations of sediment texture and TOC in the study area.

with other estuaries (table 4) and the previous studies of this wetland ecosystem (Joseph *et al.* 2008; Renjith *et al.* 2012; Akhil *et al.* 2013).

Lipids are produced by living organisms and constitute an important fraction of dissolved and particulate OM in aquatic environments (Borsheim *et al.* 1999; Burdige *et al.* 2000). It constitutes a

major portion of the labile OM and has implications on meiofauna abundance and biomass (Cartes *et al.* 2002; Gremare *et al.* 2002). Elevated levels of total lipids (range: 115.29–8450 mg/kg) reported in the present investigation reflected the productive nature and effective biological activity (Gremare *et al.* 1997; Akhil *et al.* 2013). A surplus of

Table 1. The minimum, maximum, average and spatio-temporal variation (p value – ANOVA) of general sedimentary characteristics and various biochemical components in the study area.

Parameters	Minimum	Maximum	Average	ANOVA (p value)	
				Spatial	Seasonal
Sand (%)	0.9	99.14	40.87±33.72	<0.01	0.25
Clay (%)	0.09	51.42	19.41±14.20	<0.01	<0.01
Silt (%)	0.24	86.6	39.72±24.33	<0.01	0.03
TOC (%)	0.16	6.39	2.58±1.79	<0.01	0.98
Total nitrogen (N%)	0.02	1.07	0.18±0.25	0.08	<0.01
Total sulphur (S%)	0.16	3.10	1.18±0.74	<0.01	0.64
Total protein (mg/kg)	110.67	19420	2338±3627	0.039	0.65
Total carbohydrate (mg/kg)	434.19	12839	2947±2547	<0.01	0.53
Total lipid (mg/kg)	115.29	8450	2303±1860	<0.01	0.01
Chlorophyll <i>a</i> (µg/kg)	0.36	18.49	7.55±4.91	<0.01	0.29
Chlorophyll <i>b</i> (µg/kg)	0.24	16.00	3.83±2.57	<0.01	0.17
Chlorophyll <i>c</i> (µg/kg)	0.23	26.20	4.48±3.46	0.02	0.17
Phaeophytin (µg/kg)	1.33	28.98	13.07±8.24	<0.01	0.22
TL (mg/kg)	7.18	6706	1379±1415	<0.01	<0.01
δ ¹³ C (‰)	−32.34	−25.39	−27.91±1.82	<0.01	<0.01

allochthonous OM input to the Cochin estuarine system has already been reported (Balachandran *et al.* 2003; Babu *et al.* 2006; Thottathil *et al.* 2008; Martin *et al.* 2010) and the observed data provided evidence for terrestrial input. Comparatively higher concentrations of dissolved and particulate organic carbon generated from sewage is delivered through various canals linked to Cochin estuary (Martin *et al.* 2010). The general distribution pattern of lipids (comparable with other studies – table 4), revealed a higher concentration at the industrial zone (figure 3) indicating terrestrial run-off coupled with industrial input. The riverine and fishing zones receive organic waste materials from aquaculture, agricultural activities as well as coconut retting yards (Thomson 2002; Babu *et al.* 2006; Martin *et al.* 2010), which alters the composition of sedimentary organic matter.

It is a well-known fact that proteins constitute a significant portion of labile sedimentary organics, originating from autochthonous as well as allochthonous inputs. Compared to the other studies (table 4), wide fluctuations in PRT content (range: 110.67–19420 mg/kg) were noticed in the present investigation (figure 3); with strong spatial variability ($p < 0.01$). The maximum concentration of PRT was noted at industrial zone (S14). Fish processing units situated on the banks of CES release enormous quantities of waste materials into the estuary contributing OM enriched with protein, which is ultimately adsorbed/settled in the sediment phase (Vasudevan 2000; Balasubramanian *et al.* 2012). Figure 3 clearly illustrates that riverine and industrial zones were characterized by higher levels of PRT indicating anthropogenic interventions altering the distribution pattern.

Lipid content and lipid to carbohydrate ratio (LPD/CHO) have been used as a powerful index to describe the food quality of the OM in the sediments (Fabiano and Pusceddu 1998; Gremare *et al.* 2002). It has been established that the lipid concentration in sediments is a good descriptor of the benthic trophic status (Danovaro *et al.* 1999, 2000; Dell'Anno *et al.* 2002) and the observed values were comparable with the previous reports (Joseph *et al.* 2008; Renjith *et al.* 2012). The LPD/CHO ratio ranged from 0.08 to 3.85 (figure 4a) with a maximum value at the riverine zone (S2) during POM09, which implied high nutritional value as well as the freshness of OM in the sedimentary environment. Significantly lower ratios observed during the monsoon season ($p < 0.01$) provided a clear evidence of lower productivity and higher allochthonous organic input associated with land runoff (Jacob *et al.* 2008, 2009).

PRT/CHO has been used as an index to determine the origin of OM in sediments and to distinguish between fresh and aged OM (Danovaro *et al.* 1993; Cividanes *et al.* 2002). Marked variation in PRT/CHO was seen and varied, from 0.04 (S6; PRM10) to 2.66 (S2; POM09), which coincide with the previous observations (Joseph *et al.* 2008). Figure 4(b) illustrates, lower PRT/CHO ratio (<1) at most of the stations which could be due to accumulation of higher plant debris enriched with carbohydrates (Danovaro 1996). But the enhanced PRT/CHO ratio (>1) recorded in a few stations (figure 4b) established freshly deposited detritus (Danovaro *et al.* 1993).

Estimated chlorophyll pigments exhibited a spatial variation ($p < 0.01$) and were in the range: chl-*a*: 0.36–18.49 µg/kg, chl-*b*: 0.24–16 µg/kg,

Figure 3. Seasonal and spatial variations of tannin and lignin, total carbohydrate, total proteins, total lipids and chlorophyll pigments in surface sediment of Cochin estuarine system.

Figure 4. Variations of lipid to carbohydrate ratio (a), protein to carbohydrate ratio (b), and percentage contribution of LOM to TOM (c) in surface sediments of the study area.

chl-*c*: 0.23–26.20 $\mu\text{g/kg}$. This pigment concentrations were very comparable with the other estuaries (table 4). Spatial variation of chlorophyll pigments in the surface sediments was attributed to light availability and DO content in the water column (Kowalewska and Szymczak 2001; Kowalewska *et al.* 2004; Moreno and Niell 2004). Chl-*a* content exhibited pronounced seasonal variation with its maximum in the pre-monsoon and minimum during the monsoon season. A highly significant positive correlation (table 2) with fine-grained

fraction (silt and clay) implied the effect of grain size on the pigment distribution in sediments (Colijn and Dijkema 1981; Moreno and Niell 2004). Bulk quantities of suspended particulate matter leached via river run-off, and enhanced the water column turbidity leading to reduction in solar radiation. Autochthonous water column input contributes chlorophyll to sediments (Szymczak-Zyła and Kowalewska 2007). The depleted levels of pigments during monsoon might also be due to high flushing which results in the faster removal of phytoplankton towards the coastal regions (Jyothibabu *et al.* 2006). Concentration of chlorophyll pigments in the sediments followed the trend: chl-*c* > chl-*a* > chl-*b* (figure 3). The ratio of chl-*a* to phaeopigments showed a minimum value at fishing zone (S5; 0.20 $\mu\text{g/kg}$; POM10) and maximum at the industrial zone (S15; 1.24 $\mu\text{g/kg}$; PRM10).

In most of the stations, the estimated chl-*a* to phaeopigments ratio were low (<1) and the ratio of chl-*a*/(chl-*a* + phaeopigments) ranged from 0.17 to 0.55. Phaeopigments, the early breakdown product of chl-*a* degrade more slowly and the concentration of chl-*a* to phaeopigments ratio could suggest the relative rate and time-frame of phytoplankton deposition. Combined use of these ratios suggested a rapid and recent deposition of phytoplankton in sediments (Josefson and Conley 1997; Hagy *et al.* 2005). Similarly, the close relationship (table 2) between biochemical constituents (CHO and LPD) and chloropigments in the sediments pointed out a higher contribution of phytobenthic populations and their associated detritus to the bulk organic matter (Fabiano and Danovaro 1994; Danovaro *et al.* 2000).

Aromatic polycyclic phenolic compounds such as tannin and lignin are synthesised by the vascular plants (Finar 1976; Field and Lettinga 1987; Hernes and Hedges 2000) and are transported to sedimentary environments via terrestrial run-off. Tannin and lignin form a significant fraction of refractory OM and its estimation provides valuable information on the input of terrestrially-derived organic detritus in marine systems (Lin *et al.* 2006). Tannin and lignin content displayed strong spatial and seasonal variations ($p < 0.01$) with a range of 7.18 to 6706 mg/kg. The high tannin and lignin content recorded in the study area (figure 3) might be originating from terrestrial vascular plant debris. The abundance of these unique phenolic compounds has already been published (Renjith *et al.* 2012; Akhil *et al.* 2013).

The assessment of the nature of organic matter, whether it is labile or refractory is a crucial step in organic geochemical studies and can be studied employing different biochemical compounds. The sum of all proteins, carbohydrates and lipids are defined as labile (Danovaro *et al.* 1993; Civitanes

Table 2. Correlation between sedimentary parameters in the study region.

Parameters	Sand	Clay	Silt	TOC	N	S	PRT	CHO	LPD	Chl-a	Chl-b	Chl-c	Phe	TL
Sand	1													
Clay	-0.78	1												
Silt	-0.93	0.49	1											
TOC	-0.33	0.25	0.32	1										
N	-0.18	0.2	0.13	0.41	1									
S	-0.43	0.38	0.37	0.58	0.6	1								
PRT	-0.07	0.03	0.08	0.52	0.42	0.4	1							
CHO	-0.19	<i>0.25</i>	0.12	0.68	0.48	0.48	0.6	1						
LPD	-0.41	0.46	0.3	0.62	0.47	0.56	0.37	0.54	1					
Chl-a	-0.41	0.39	0.34	0.41	<i>0.27</i>	0.54	0.07	0.35	0.44	1				
Chl-b	<i>-0.25</i>	<i>0.25</i>	0.2	0.41	0.16	0.39	0.04	<i>0.27</i>	0.45	0.83	1			
Chl-c	-0.13	0.12	0.011	0.38	0.11	<i>0.27</i>	0.07	<i>0.24</i>	0.43	0.66	0.95	1		
Phe	-0.4	0.38	0.33	0.34	0.25	0.48	0.06	<i>0.3</i>	0.37	0.94	0.72	0.52	1	
TL	-0.05	-0.04	0.1	0.5	0.42	0.35	0.61	<i>0.52</i>	0.49	0.12	0.17	<i>0.23</i>	0.05	1

Note: Correlation significant at 0.01 level are shown in bold and correlation significant at 0.05 level are shown in italics.

Table 3. Trophic status of the study area (season-wise).

Zone	POM09	PRM09	MON09	POM10	PRM10
Riverine	Eutrophic	Eutrophic	Oligotrophic	Eutrophic	Eutrophic
Fishing	Mesotrophic	Mesotrophic	Oligotrophic	Mesotrophic	Mesotrophic
Sewage/tourism influenced	Mesotrophic	Mesotrophic	Mesotrophic	Mesotrophic	Eutrophic
Industrial	Eutrophic	Eutrophic	Eutrophic	Mesotrophic	Eutrophic

and Souza 2003). Labile fraction denotes the easily assimilable portion of organic matter that is easily available for the use of aquatic organisms including benthos. The labile organic matter (LOM) content in sediments recorded a remarkable variation from 746.47 to 36847 mg/kg; its contribution to TOM varied from 4.85 to 45.19%. The river and industrial zones (figure 4c) indicated higher contribution of LOM to TOM and the elevated values establish enhanced productivity, coupled with external supply of terrigenous materials. Previous studies from the CES recorded contribution of LOM to TOM ranging from 9.43–31.10% (Joseph *et al.* 2008), suggested the fact that a significant fraction of TOM represented refractory material.

Characterization of trophic state in aquatic ecosystems is necessary for understanding food web linkages as well as biogeochemical features and subsequently water quality (Smith 2003). Like other ecosystems, estuaries have biotic communities that depend on carbon resources to fuel food webs and maintain the organisms that live in them. Generally trophic status are categorised as oligotrophic (unproductive), mesotrophic (intermediate productivity) and eutrophic (highly productive). Trophic state can be influenced by light, external carbon source, nutrients, hydrology and food web structure (Dodds and Cole 2007). The indiscriminate and unscientific application of fertilisers,

industrial input and domestic sewage has introduced bulk quantities of nutrients into the estuary, which affected the food web structure and alterations in trophic state. Trophic state assessment was carried out based on biopolymeric carbon (BPC) and the algal contribution to BPC (Pusceddu *et al.* 2011). This methodology categorise the estuarine stations as follows: eutrophic (BPC > 3 mgC/g, algal fraction < 12% of BPC), mesotrophic (BPC = 1–3 mgC/g, algal fraction = 12–25% of BPC) and oligotrophic (BPC < 1 mgC/g, algal fraction > 25% of BPC). Algal contribution to BPC was calculated as the percentage of chl-a to BPC concentrations, after converting chl-a concentration into carbon equivalents (chl carbon) using a mean value of 40 (Pusceddu *et al.* 2009). The ratio of chl carbon to chl-a in sediments usually vary from 10 to higher than 100 (De Jonge 1980) and using this mean value, comparison of the present data with literature information from other marine and coastal areas was possible (Pusceddu *et al.* 1999, 2009, 2011).

Based on these criteria, present investigation ranked the stations as mesotrophic or eutrophic. Seasonal variation was recorded in the benthic trophic state of the estuarine system. The riverine (except MON09) and industrial zones (except POM10) were eutrophic. Mesotrophic character was observed in the fishing (except MON09) and

Table 4. Comparison of present study with bulk sedimentary parameters from different estuaries in the world.

Study region	LPD (mg/kg)	PRT (mg/kg)	CHO (mg/kg)	Pigments ($\mu\text{g/kg}$)	$\delta^{13}\text{C}$ (‰)	TOC/N	Reference
South-eastern Arabian sea	900–5100	100–7300	400–3500	–	–	–	Ramya <i>et al.</i> (2013)
East coast of India	–	–	2800–4710	–	–23.2 to –19.6	15–23	Kumar <i>et al.</i> (2013)
Cochin estuary	41.50–3160	24.48–2600	166–6339	Chl- <i>a</i> : 220–37800 Chl- <i>b</i> : BDL–16710 Chl- <i>c</i> : BDL–8970 Phe: 360–64520	–28.25 to –24.73	0.73–33.62	Renjith <i>et al.</i> (2012)
Rio de la Plata estuary	500–8350	1080–16370	290–8860	Chl- <i>a</i> : $0.1 * 10^{-6}$ – $11.6 * 10^{-6}$ Phe: $1.7 * 10^{-6}$ – $35 * 10^{-6}$	–	–	Venturini <i>et al.</i> (2012)
Cochin estuary	–	–	–	–	–27.5 to –21.7	7–21	Gireeshkumar <i>et al.</i> (2012)
Pichavaram mangrove – estuarine sediments, India	–	–	–	–	–23.2 to 5.1	12.3	Ranjan <i>et al.</i> (2011)
Pearl river estuary	–	–	–	–	–25.1 to –21.3	6.50–13.30	He <i>et al.</i> (2010)
Pearl river delta and estuary	–	–	–	–	–25 to –21	6.8–15.2	Fengling <i>et al.</i> (2010)
Pichavaram estuary	–	–	–	–	–28.92 to –25.34	–	Prasad and Ramanathan (2008)
Cochin estuary	312–2815	205–1924	250–1229	–	–	4.80–10.62	Joseph <i>et al.</i> (2008)
Mundaka estuary	300–5000	BDL–16700	200–5700	–	–	–	Cotano and Villate (2006)
Yangtze estuary, China	–	–	–	Chl- <i>a</i> : $0.05 * 10^{-6}$ to $8.01 * 10^{-6}$	–29.8 to –26.0	1.6–5.5	Liu <i>et al.</i> (2006)
Chunnambar, India	–	–	–	–	–23.3 to –24.5	–	Bouillon <i>et al.</i> (2004)
Winyah Bay, SC, USA	–	–	–	–	–28 to –23	5–45	Goni <i>et al.</i> (2003)
Harney river estuary, Florida	–	–	–	–	–28.9 to –19.0	–	Hernandez <i>et al.</i> (2001)
Lower St. Lawrence estuary	820–1470	110–400	7580–10700	–	–	–	Colombo <i>et al.</i> (1996)
River estuary (Tyrrhenian Sea)	2.9–12.6	250–1670	350–1890	Chl- <i>a</i> : 90–1500 Phe: 30–1900	–	–	Fabiano and Danovaro (1994)
Cochin estuary	115.29–8450	110.67–19420	434.19–12839	Chl- <i>a</i> : 0.36–18.49 Chl- <i>b</i> : 0.24–16 Chl- <i>c</i> : 0.23–26.20 Phe: 1.33–28.98	–24.73 to –46.43	0.57–26.75	Present study

BDL: below detectable limit, * indicate multiplication sign.

sewage/tourism influenced zones (except PRM10) during the investigation (table 3) period. The wide fluctuations in trophic status could be attributed to the input of large quantities of allochthonous OM into the estuary (Thomson 2002; Balachandran *et al.* 2003; Babu *et al.* 2006; Thottathil *et al.* 2008; Martin *et al.* 2010). The estuary receives heavy fresh water influx during summer monsoon (Srinivas *et al.* 2003) and the consequent run-off results in the large amount of OM to this estuary (Balachandran *et al.* 2003). Moreover, enriched levels of dissolved and particulate OM have been recorded from the central part of the estuary (Martin *et al.* 2010) which clearly reflected sewage input from various outlets of Cochin city. The eutrophication induced changes in the benthic community structure was also recently reported by Martin *et al.* (2011). Furthermore, the alteration in trophic status directly affects the ecological balance and biogeochemical cycles of carbon and associated elements.

In order to achieve more information on the sources of the OM and their transformation processes, elemental and stable carbon isotope ratios were used (Gearing *et al.* 1977; Tan *et al.* 1991; Thornton and Mc-Manus 1994; Meyers 1997; Mitchell *et al.* 1997; Andrews *et al.* 1998; Graham *et al.* 2001; Bianchi *et al.* 2002). TOC/N ratios have been used as efficient tracers of OM based on the fact that marine and terrestrial derived OM have a TOC/N ratio of 5–8 and >15, respectively

(Meyers 1997). Apart from other indices, TOC/N ratio displayed its minimum (0.57) at S10 and maximum (26.75) at S7. Intermediate values of TOC/N ratio signalled a mixed contribution of both autochthonous and terrestrial OM to the estuarine sediments (Muri *et al.* 2004) and the data was comparable with previous studies (table 4).

The application of $\delta^{13}\text{C}$ was based on the assumption that marine organic matter typically possesses values for terrestrial C3 plants (-26 – -28‰) and phytoplankton (-19 – -22‰) (Gearing *et al.* 1977; Meyers 1997; Bianchi *et al.* 2002). $\delta^{13}\text{C}$ of bulk organic matter obtained in the present investigation varied from -32.34 to -25.39‰ . The riverine (S1, S2, S3, S4) and industrial zones (S13, S14 and S15) recorded more depleted $\delta^{13}\text{C}$ values, suggesting a major contribution of terrestrial higher plant debris to sedimentary organic matter. Biochemical constituents and bulk organic matter parameters like stable carbon isotope ratios estimated in present investigation were in good agreement with earlier reports (table 4).

The statistical analysis (table 2) revealed a positive correlation between fine grained fractions (silt and clay) with various biochemical constituents. The strong relationships exhibited by TOC, N and S with CHO, PRT, LPD and other variables pointed towards the adsorption and diagenetic process controlling the distribution of the biochemical components in the sedimentary environment. Inter-relationship among the biochemical components

Figure 5. Canonical correspondence analysis showing the distribution and association of various biochemical components studied in the Cochin estuarine system.

with each other points towards a common source and similar behaviour in the estuarine environment. Significant correlation of carbohydrates with chloropigments in sediments pointed out the contribution of phytobenthic populations and derived detritus to the total OM.

Canonical correspondence analysis (CCA), a multivariate extension of weighed averaging ordination was used in the present study to relate the distribution of different biochemical components to general sedimentary parameters. The length of the arrows (sedimentary parameters) and their orientation indicates their relative importance and approximate correlations to the axes. The arrows point out in the direction of increase of the sedimentary parameters.

Figure 5 revealed higher concentration of phaeopigments in the riverine (S3-MON09), fishing (S7-PRM09, S6- and S7-POM10, S5-PRM10), sewage/tourism influenced (S10-PRM09 and POM10) and industrial zones (S11, S13-PRM09). Similarly lipids were more concentrated in fishing (S6-PRM10) and sewage/tourism influenced zones (S8-PRM09 and PRM10, S9-PRM10). Carbohydrates were more abundant at the riverine (S1, S2-PRM10) and fishing zones (S6-MON09). Proteins were concentrated at riverine (S1-POM10) and industrial zones (S12-PRM10, S15-PRM09). Further, CCA analysis established the fact that, protein distribution was influenced by changes in N, S and TOC (figure 5); while phaeopigments did not show any relation with sedimentary parameters. It could also be deduced that the dispersal pattern of carbohydrates and lipids in sediments were controlled by pH and fine grained fractions (silt and clay) of the sediment.

4. Conclusion

Texture analysis implied the predominance of silt and clay in the estuarine sediments. The TOC/S ratios in the majority of the stations inferred periodic anoxia. The high lipid content and LPD/CHO ratio not only reflected the quality of OM to support benthic fauna, but a better preservation of lipid compounds in the sedimentary environment. Lower PRT/CHO ratio suggested a detrital heterotrophic environment in the study area. Biopolymeric carbon and the algal contribution to BPC provided important information on the better understanding of the trophic status. Estimated TOC/N ratios implied the combined input of both terrestrial and autochthonous organic matter to sediments. The more depleted $\delta^{13}\text{C}$ value of bulk sedimentary organic matter implied terrestrial input of vascular plant debris, which was supported by higher concentrations of tannin and

lignin. Chl-*a*/phaeopigment ratio and chl-*a*/(chl-*a* + phaeopigment) ratio, revealed rapid and recent deposition of phytoplankton detritus to sediments. Grain size, nutrients and total organic carbon content had substantial influence on the distribution of the biochemical composition of sediments. Canonical correspondence analysis revealed that the association of variables and their distribution/accumulation trends within the various zones of the estuarine ecosystem. Molecular level characterization (biomarker approach) is recommended to achieve more specific information on the degradation status of OM in this complex ecosystem.

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