

Core sediment biogeochemistry in specific zones of Cochin Estuarine System (CES)

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Geochemical composition is a set of data for predicting the climatic condition existing in an ecosystem. Both the surficial and core sediment geochemistry are helpful in monitoring, assessing and evaluating the marine environment. The aim of the research work is to assess the relationship between the biogeochemical constituents in the Cochin Estuarine System (CES), their modifications after a long period of anoxia and also to identify the various processes which control the sediment composition in this region, through a multivariate statistical approach. Therefore the study of present core sediment geochemistry has a critical role in unraveling the benchmark of their characterization. Sediment cores from four prominent zones of CES were examined for various biogeochemical aspects. The results have served as rejuvenating records for the prediction of core sediment status prevailing in the CES.

1. Introduction

Estuaries are commonly described as semi-enclosed bodies of water, situated at the interface between land and ocean, where seawater is measurably diluted by the inflow of freshwater (Hobbie 2000). These dynamic ecosystems have the highest biotic diversity and production in the world. Recent estimates indicate that 61% of the world population lives along the coastal margin (Alongi 1998). Impacts of demographic changes in human populations have clearly had detrimental effects on the overall biogeochemical cycling in estuaries. Nutrient enrichment is perhaps the most widespread problem in estuaries around the world (Howarth *et al.* 2000, 2002). Understanding the biogeochemical and physical processes that play an important role in regulating the chemistry and biology of estuaries is fundamental to evaluate the complex management issues (Hedges and Kiel 1995; Middelburg *et al.* 1996; Bianchi *et al.* 1999a; Hobbie 2000). Biogeochemical cycles involve the

interaction of biological, chemical as well as geological processes that determine sources, sinks, and fluxes of elements through different reservoirs within the ecosystems.

Cochin Estuary, one of the largest tropical estuaries of India is facing gross pollution problems following the release of untreated effluents from industries and domestic sectors. The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutilles plant, zinc smelter plant, insecticide manufacturing unit and organic chemical plant. Reclamations over the past several decades have resulted in considerable shrinkage (40%) of the Cochin Estuary (Gopalan *et al.* 1983). Further, construction of hydraulic barriers on the northern and southern limbs of the estuary to prevent saline intrusion into the upstream agricultural fields has imposed severe flow restrictions and increased sedimentation in the estuary (Menon *et al.* 2000). The developmental activities in and around Cochin Backwater System have added to the

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complexities and environmental dilemmas in this coastal niche. The rapid growth in the region accompanied by very high population growth, housing shortages, haphazard industrial and commercial improvement along transportation corridors have greatly increased the problems of urban development. The hydrologic changes in these water bodies were mainly on account of port extension, large scale land reclamation, construction of dams on the rivers that discharge into the backwaters and diversion of water flows by the construction of spillways, etc. For a long period there were no pollution control regulations and the untreated effluents including those from heavily polluting industries were being discharged into the backwaters. Geochemical studies of sediment core profiles describe the degree of contamination by encapsulating various amounts of biogenic compounds (including biogenic alkanes, sterols, carbohydrates, protein, hydrocarbons, etc.) and provide furthermore useful information on the changes in the quality of the sediments from past period (Faganelli *et al.* 1987; Holm 1988; Karbassi and Shankar 2005; Al-Juboury 2009; Ahmad *et al.* 2010; Chibunda *et al.* 2010). The present investigation also infers the quality of the biogeochemical constituents in

the core sediments of the Cochin estuary which would strengthen the environmental dynamics of the studied site.

2. Study area

The study area was divided into three zones, *viz.*, south, middle, and north (figure 1).

2.1 South zone

The zone originated from the southern bough of the fresh water river Moovattupuzha. One sediment core (SS₁) was taken from this zone which is far from industrial effluents.

2.2 Middle zone

This zone was considered as two segments and the first site (MS₁) is well regulated by a bund (namely Thannirmukham) which was constructed in order to prevent the intrusion of salt water into the paddy fields. The bund remains open during the monsoon season.

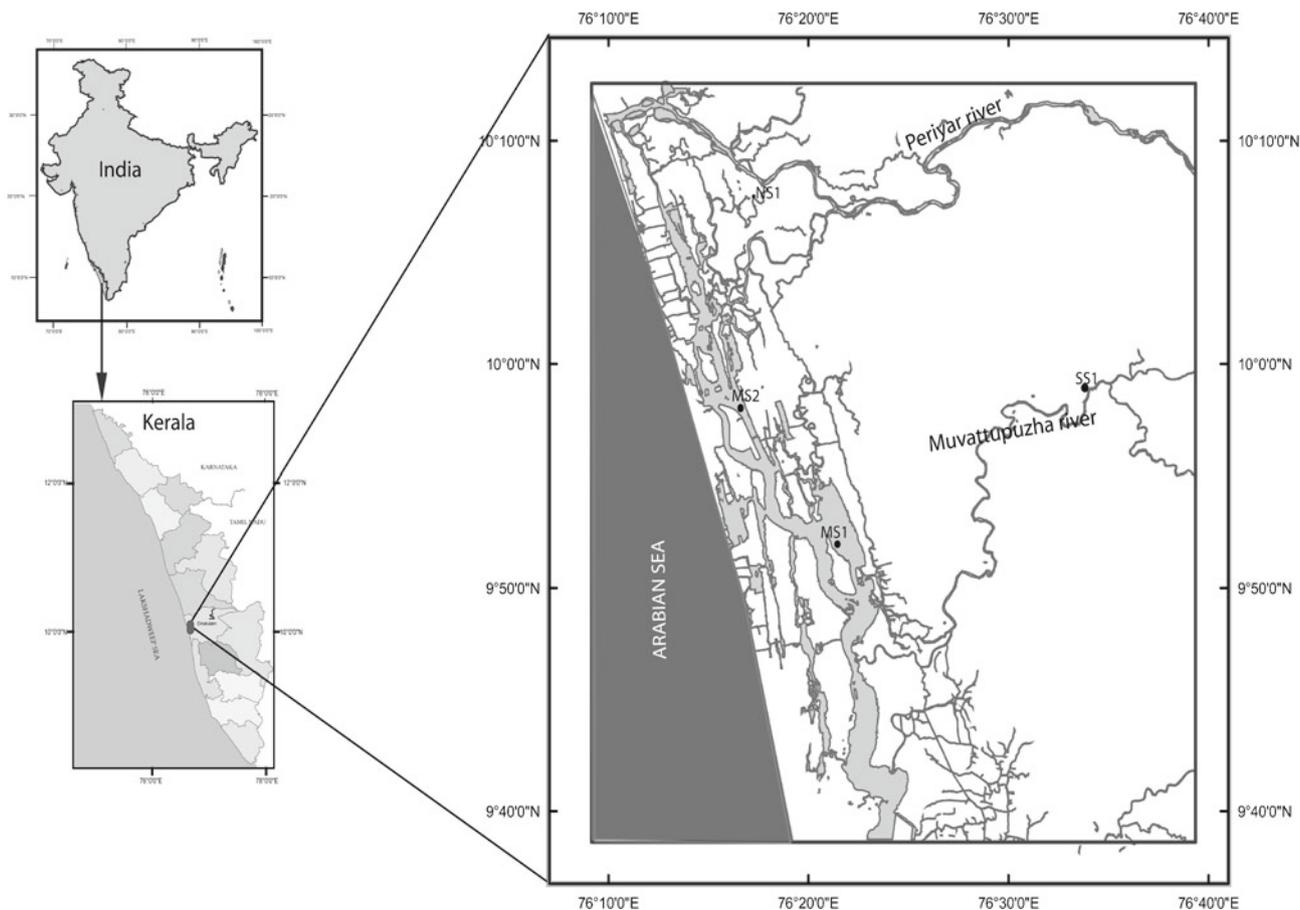


Figure 1. Location map of the study area.

The second site (MS₂) was at Vallarpadam. With the advent of ICTT project, this area has become the backbone of the economy of Kerala State. It focuses on the enhancement of containerization in India, resulting in the improvement of trade and economic growth. Widespread activities like dredging and piling, along with anthropogenic inputs are carried out frequently. This zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion thereby making cradle grounds for diverse types of flora and fauna.

2.3 North zone

This zone instigate from the industrial locale of Periyar – the life line of Kerala. One sediment core (NS₁) sample was collected from this zone. Large scale industries on the river bank discharge effluents directly into these waterways resulting in the accumulation of varying amounts of nutrients in the Periyar River.

3. Sampling and methods

The cores were collected at low tide by pushing a hand-held PVC core (150 cm long with a diameter of 6.3 cm) in November 2009 by a diver at the above-mentioned three zones of the CES, in varying depths (1–3.50 m) of the water body. The different length of the core obtained were 45 cm (SS₁), 55 cm (MS₁), 63 cm (MS₂) and 23 cm (NS₁). The sediment cores were sliced into 3 cm segments, transferred to plastic vessels and each subsample constitutes 15, 19, 21 and 10 for SS₁, MS₁, MS₂ and NS₁ cores, respectively. The pH (Thermo Orion 420A+ model) of the subsamples was immediately measured and then they were frozen at 4°C for further analysis. These subsamples were air dried, finely powdered and used for further chemical analysis.

The sediment samples were mixed and subjected for the analysis of tannin and lignin, lipid, carbohydrate and protein. Textural characteristics (sand, silt, and clay) and quantification of OM (protein, lipid and carbohydrate) were carried out by standard procedure. Texture was determined using pipette analysis (Lewis 1984). Total Organic Carbon (TOC) was processed by treating the samples with 1 M HCl to remove the carbonates and repeated two/three times in order to ensure the complete exclusion of carbonates. Samples were washed with Milli-Q water to remove salts and finally freeze dried. Organic carbon was determined using TOC analyzer (Elementar Vario Select, Germany). Samples were run with blank cups in

order to correct the carbon associated with the tin cups. Standard sediments supplied by Elementar Vario Select, Germany, were used for calibration in the TOC analyzer. The detection limit for OC is 0.06%. Total proteins were determined using the method of Lowry *et al.* (1951). Carbohydrate estimation was done by Phenol-Sulphuric acid method (Dubois *et al.* 1956). Tannin and lignin were batch-extracted from the sediments with 0.05 M NaOH solution for 90 minutes and filtered. To 5 ml aliquots of filtrates, 1 ml of citrate solution was added followed by 1 ml folin reagent and 10 ml carbonate tartarate reagent and kept it for 30 minutes. The optical density was measured at 765 nm (APHA 1995; Jose *et al.* 2008). Total lipid was estimated by the Sulphophosphovanillin method (Barnes and Blackstock 1973). All the analyses were carried out in triplicate and the average was reported. Protein, carbohydrate and lipid concentrations 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 total of protein, carbohydrate and lipid carbon were referred to as biopolymeric carbon (BPC) (Fichez 1991; Fabiano *et al.* 1995) and the study accounted accordingly. Sediment samples for the pigment analysis were immediately collected in 15 cm plastic vials for preservation by direct freeze drying. For the analysis of sedimentary chlorophyll and their degradation products, 0.5 g of freeze-dried sample was added to the glass centrifuge tube with 90% acetone and the mixture was sonicated at 5 atm for 30 sec to disrupt the cells and kept in dark at 4°C for nearly 5 hrs in order to ensure the complete extraction of the pigment. The mixture was then centrifuged at 3000 rpm to separate the pigment solvent complex from the remaining sediment. This process was repeated until the colour of the extract was clear. The supernatant liquid was then transferred to UV spectrometer (GENESYS 10 UV Thermo spectra) for further analysis. The concentrations of chlorophyll, pheophytin and carotenoid pigments were measured by the spectrophotometric method (Parsons *et al.* 1984; APHA 1995; Aneeshkumar and Sujatha 2012). All the four core sediment standard deviation varied for lipid, tannin and lignin, carbohydrate, pigment and texture as 2.1–5.6; 0.1–0.6; 0.4–10.4; 0.2–1.9; 0.1–30.4 and 5.7–31.3, respectively. Elemental compositions, CHNS of the samples were determined using Vario EL 111 CHNS Analyzer. The Principal Component Analysis (PCA) method, which enables a reduction in data and description of a given multidimensional system by means of small number of new variables, has been applied to the data. The data processing was carried out using the software Statistica 6.0.

4. Results

4.1 Sediment characteristics

Colour, pH and texture for each core sediment are discussed.

4.1.1 Core SS₁

Varying colour combination in core sediment was observed. Up to 10 cm it showed blackish brown, brownish black till 40 cm and then blackish brown. Values of pH ranged from 5.4 at 3 cm depth to 7.2 at 42 cm depth and it was found to exhibit an increasing trend with minor fluctuations from surface to bottom. Clay content dominated in this core and showed a variation ranging from 3.2% to 97.8%. Along the core, as depth increased clay fraction also increased.

4.1.2 Core MS₁

The whole core appeared blackish brown in colour. Values of pH ranged from 7 to 8. Sand content dominated in this core. Relative textural distribution was in the order; sand > clay > slit.

4.1.3 Core MS₂

Mixed black and grey colour at 0–36 cm and uniform black colour up to 63 cm were noted. Values of pH ranged from 7.9 at 63 cm depth to 8.7 at 9 cm depth and it exhibited a decreasing trend with minor fluctuations from surface to bottom. Sand content was intensified in this core. The textural variation was in the order; sand > clay > slit.

4.1.4 Core NS₁

The entire core were blackish brown in colour. Values of pH ranged from 6.1 to 6.6. The highest pH at 6 cm depth and lowest at 21 cm depth. Clay content varied between 1.9% and 85.4%. Along the core as depth increased sand content also intensified.

5. Organic matter (OM)

The distribution and variation of OM in different core sediments are illustrated as follows.

5.1 Core SS₁

Percentage of TOC ranged from 2.7 to 3.8, showing the lowest and the highest at a depth of 27 cm and 12 cm, respectively. Total carbohydrate concentration ranged from 4.7 to 11.7 mg/g. Maximum and minimum concentrations were observed

at 6, 18 cm depths, respectively. Towards the lower end of the core, concentration of carbohydrate was found increased. Concentration of total protein ranged from 0.9 to 7.1 mg/g and concentration of protein was fairly high at middle portions. The maximum was observed at a depth of 6 cm and minimum was at 39 cm. Concentration of lipid was prime at the top portions and lowest towards bottom. At 39 cm depth the concentration reached maximum (34.1 mg/g) and again decreased to 15.1 mg/g at 45 cm. Concentration of tannin and lignin ranged from 1.0 to 1.6 mg/g. The highest was noted at 39 cm depth and the lowest at 18 cm depth. Relative OM distribution was in the order: lipid > carbohydrate > protein > tannin and lignin (figure 2).

5.2 Core MS₁

TOC decreased from top (0.7%) to bottom (0.6%) of the core. Total carbohydrate concentration ranged from 0.7 to 9.1 mg/g. The lowest concentration was observed at the depth, 24 cm and the highest at 39 cm. Concentration of carbohydrate was enriched at the bottom of the core. Concentration of total protein ranged from 0.2 to 1.6 mg/g at 3 and 24 cm depth, respectively. Concentration of protein was the maximum at the middle portion and almost constant towards the bottom. Total lipid concentration ranged from 1.3 to 9.1 mg/g and lowest at 45 cm depth and the highest at 39 cm depth. Concentration of lipid was enriched from the surface to the middle portions of the core. The tannin and lignin concentration ranged from 0.09 to 0.46 mg/g. The lowest concentration was observed at 3 cm depth and the highest at 54 cm depth. Concentration of tannin and lignin augmented towards the bottom of the core. Relative OM distribution was in the order; lipid > carbohydrate > protein > tannin and lignin (figure 2).

5.3 Core MS₂

Percentage of TOC ranged from 0.7 to 1.2. The maximum was noted at 24 cm depth and minimum at 6 cm of the core. TOC values increased towards the bottom of the core. Concentration of total carbohydrate ranged from 0.9 to 1.6 mg/g. The lowest concentration was observed at 54 cm depth and the highest at 36 cm depth. Concentration of carbohydrate was enriched in the surface and middle portions of the core. Total protein concentration ranged from 0.2 to 0.8 mg/g. The lowest concentration was observed at 6 cm depth and the highest at 29 cm depth of the core. Concentration of protein increased from the middle to the bottom

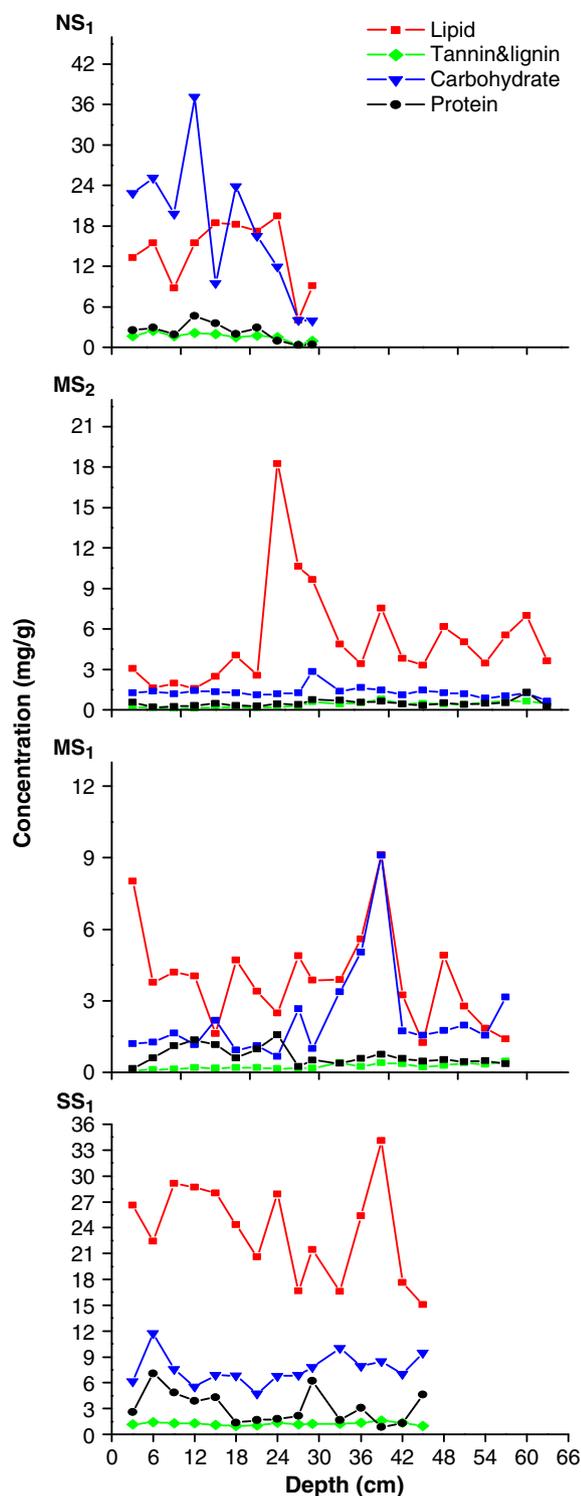


Figure 2. Distribution profile of organic matters (mg/g) in different cores.

portions of the core. Total lipid concentration ranged from 1.6 to 18.3 mg/g. The lower concentration was observed at the depth of 12 cm and the higher at 21 cm depth. Lipid concentration was the highest in the middle portions of the core. Concentration of tannin and lignin ranged from 0.1 to 0.8 mg/g. The lowest

concentration was observed at 9 cm depth and the highest concentration was at 39 cm depth of the core. Concentrations of tannin and lignin were found increasing towards the bottom portions of the core. Relative OM distribution was in the order: lipid>carbohydrate>protein>tannin and lignin (figure 2).

5.4 Core NS₁

Percentage of TOC ranged from 0.6 to 2.9. The maximum was noted at 12 cm depth and the minimum at 27 cm of the core. In this core the amount of all the OM were drove upon same manner. Concentration was the highest in middle portions and the lowest in bottom portions of the core. Concentration of the total carbohydrate ranged from 3.9 to 37.1 mg/g. Concentration of total protein ranged from 0.3 to 4.6 mg/g. Total lipid concentration ranged from 4.0 to 19.5 mg/g and finally the tannin and lignin content ranged from 0.3 to 2.4 mg/g. The relative OM distribution was in the order: carbohydrate>lipid>protein>tannin and lignin (figure 2).

6. Discussion

Estuaries are highly dynamic and influenced by strong tidal action, entangled with fresh water and coastal discharges. A number of investigations in recent years have shed light on the varied nature and character of estuarine and mangrove sediments in and around Cochin estuary (Geetha *et al.* 2008; Manju *et al.* 2008; Niffy Benny 2009; Deepulal *et al.* 2011; Aneeshkumar and Sujatha 2012). The present study deals with the first detailed research work on core sediment biogeochemistry in the specific zones of Cochin estuarine system. In sediments, a wide variety of organic carbon forms are present and they range from freshly deposited litter to highly decomposed forms such as humus. The quality of organic matter in sediments is critical to the partitioning and bioavailability of sediment associated contaminants. Influence of total organic matter (TOM) in sediments is important to assess the fate, transport, deposition and retention of various inorganic and organic constituents. The high organic carbon associations which coincided with the high clay contents in the southern and northern parts of the estuary is attributed to the enhanced adsorption of organic carbon onto the clay minerals in the low salinity regimes (figure 2a). Lipid is one of the major biochemical compound produced by living organisms and constitute an important fraction of dissolved and particulate OM (Skoog and Benner 1997; Borsheim *et al.* 1999; Burdige *et al.* 2000). Besides, they are consumed by microhetero-

tops in both fresh water and marine ecosystems and contribute essentially to the bacterial production (Rich *et al.* 1996). Its concentrations have been associated with the most labile fraction of sedimentary organics and it is considered the best descriptor of meiofauna abundance and biomass, over enzymatically hydrolysable aminoacids or protein contents (Gremare *et al.* 1997; Fabiano *et al.* 1995; Gremare *et al.* 2002). Elevated levels of lipid concentration found at three cores (SS₁, MS₁ and MS₂) indicates the biological activity associated with the productive nature of the environment (figure 2). Prevalence of carbohydrate concentration in the northern zone (NS₁) could be attributed to the anthropogenic input and the death and decay of aquatic organisms and floating plants. In the present study, the carbon normalized value was suggestive of its terrestrial origin. Proteins are the most important nitrogen-bearing compound in most of the organisms. The study revealed that concentration of protein accounted was fairly high at SS₁ core and maximum at 6 cm depth (7.1 mg/g). Both carbohydrates and protein serve as structural and storage components and comprise of up to 40% of the OM in the marine niche and 75% of the OM in terrestrial organisms (Aspinall 1983; Parsons *et al.* 1984; Biersmith and Benner 1998). Tannins and lignins are high molecular weight polycyclic aromatic compounds which are widely distributed throughout the plant kingdom (Schnitzer and Khan 1972; Finar 1976; Field and Lettinga 1987). These compounds are highly resistant to biological degradation and have a great potential to damage the aquatic environment. The identification and quantification of these compounds in these marine environment infers the importance of land-derived organic detritus. Concentration of tannins and lignins was found higher at cores collected from the northern and southern regions, and it establishes the character of allochthonous origin. The weak flow and the huge input of industrial/agricultural waste in the northern and southern parts of the estuary result in high organic input in the study area. Decreasing trends of organic carbon detected in the middle zone may be due to strong rectilinear current, which maintains an effective flushing. Organic matter has significant relation with fine fraction of the sediment. In the top sections of the core concentration of protein, lipid and carbohydrate were found intensified in the northern (NS₁) and southern (SS₁) regions, and diminished in the core samples obtained from the middle zone (MS₁ and MS₂). Mid-portions of the cores NS₁, MS₁ and MS₂ were enriched with organic matters. In the southern zone (SS₁), concentration of these OM was deficient. Bottom sections of the cores showed decrease in the concentration of OM in the

cores NS₁, MS₁ and MS₂, whereas SS₁ revealed a heavier input of these organic matters. These observations confirmed the dependence of texture on the modification of sediment OM.

For the past several years sedimentary plant pigments have been studied and proved to be a valuable indicator of paleoecology and so the pigment parameter was also included in the study. The concentration of pheophytin pigment subjected in three cores (MS₁, MS₂ and NS₁) were highlighted (figure 3). The highest concentration (96.3 mg/kg) of pheophytin was observed in NS₁ core at a depth of 6 cm and towards the bottom, concentration was below detectable level due to low adsorbing nature of the sandy sediment. In rest of the two cores, pheophytin content dominated in the bottom portions of the sediment core. According to Dell'Anno's *et al.* (2002), the predominance of pheopigments might be attributed to high turbidity, chemical contamination or other factors affecting photosynthetic potential of the primary producers. Generally carotenoids hold the largest potential for identifying the phototropic community contributing to the sediment record due to their taxonomical specificity and high stability in relation to other pigments. The higher concentration of carotenoid (40.7 mg/kg) detected (figure 3) in the fresh water augmented core, SS₁ (at 36 cm depth) also confirmed the above concept (figure 2a).

Protein-carbohydrate ratio (PRT:CHO) is used as an index to evaluate the origin of material present in sediments and to determine the age of sedimentary organic matter (Cividanes *et al.* 2002). This ratio was generally higher in estuarine sediments which point to the presence of low dead organic matter accumulation, probably due to the vibrant condition of estuaries. In the present study this ratio showed an average value of 0.42, 0.50, 0.4 and 0.1 in SS₁, MS₁, MS₂ and NS₁ cores, respectively. Even though the middle zone is subjected to strong hydrodynamic conditions, sediments from this region also showed less PRT:CHO value. This may be due to the influence of anthropogenic inputs and rapid development activities in and around the study area. Low protein-carbohydrate ratios suggest the presence of aged OM and the role of protein as a potentially limiting factor for benthic consumers. Less dynamic nature of waters in northern and southern parts of the study area also caused low protein-carbohydrate ratio. Earlier report suggests the dominance of carbohydrate and lower PRT:CHO ratio is a typical feature of detrital heterotrophic environments (Danovaro 1996). Lipid-carbohydrate ratio (LPD:CHO) showed an average value of 3.3, 2.4, 4.2 and 1.1 in SS₁, MS₁, MS₂ and NS₁ cores, respectively, which in turn reflects energetic (food) quality of the organic

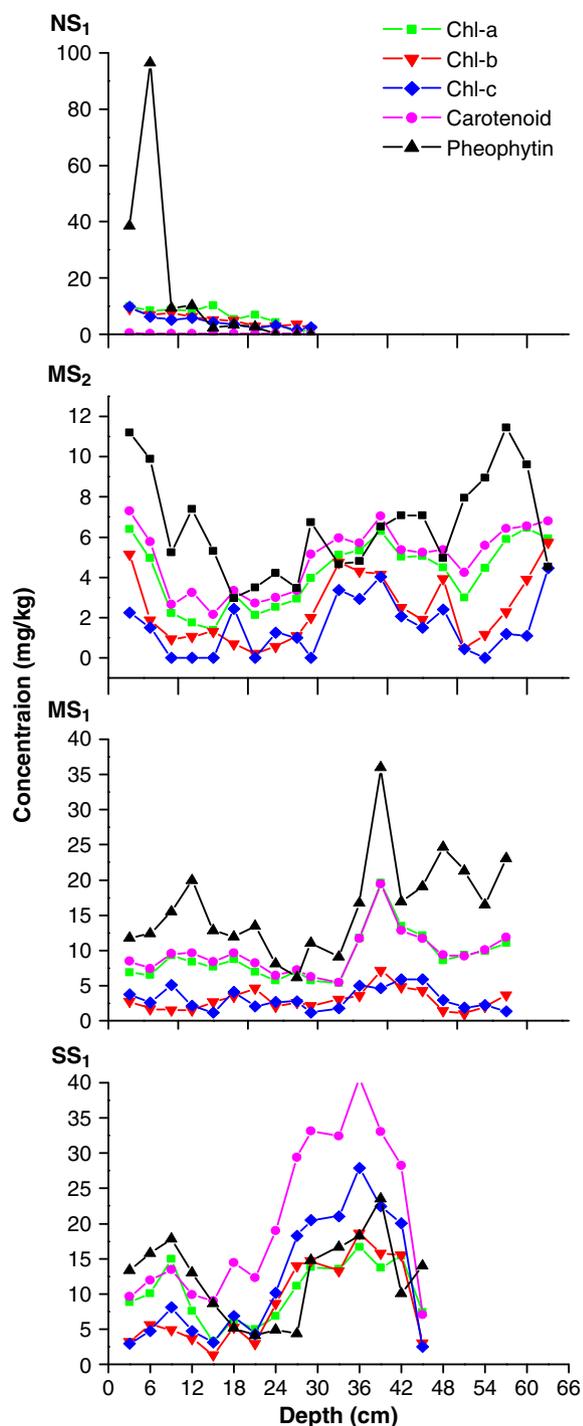


Figure 3. Variation pattern of pigments (mg/kg) in cores.

contents in the study area and well supports the earlier literatures (Gremare *et al.* 1997, 2002; Fabiano and Pusceddu 1998). Elevated value (15.758) was found in MS₂ core at a depth of 21 cm. Percent average of BPC was in the order 2.23, 0.42, 0.47 and 1.9 in SS₁, MS₁, MS₂ and NS₁ cores, respectively. The correlation analysis of various biogeochemical parameters of sediment cores was shown in tables 1–4. In core SS₁, biopolymeric carbon (BPC) showed a high significant correlation with

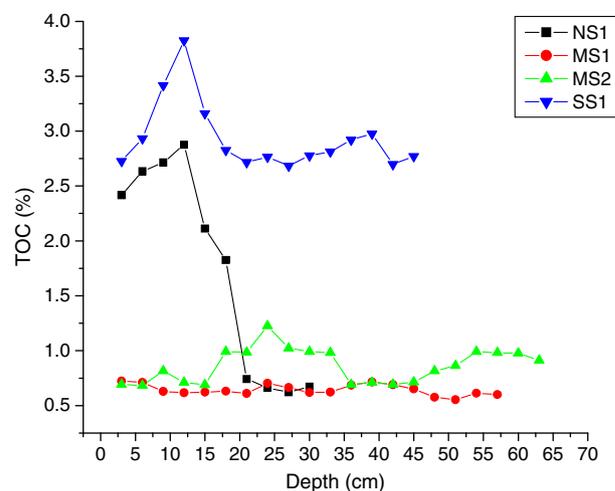


Figure 4. Distribution pattern of TOC (%) in different cores.

lipid followed by tannin and lignin, and establishes them as the major contributors to BPC. A well momentous correlation of clay with chl-*a* and pheo pigments was also noticed. In core MS₁, BPC had high significant correlation with lipid followed by carbohydrate. These observations suggest that lipid and carbohydrate also become a major contributor of BPC. A significant correlation of clay with carbohydrate, chl-*a*, chl-*b*, carotenoid and pheophytin was also observed. Generally carbohydrate has high affinity for the fine grained sediments, which constitute clay particles with increased surface area per unit weight for the absorption of OM. OM present in the sediments is found in the form of aggregates that are surrounded by clay particles. In core MS₂, BPC exhibited a significant correlation with lipid. In core NS₁, BPC had significant positive correlations with lipid, tannin and lignin, carbohydrate, protein and clay, indicating an equal contribution of all organic matter to BPC. A significant correlation was observed between BPC and clay. It was found that there is a positive correlation between the proportions of clay and OM in the aggregates and degradation of OM.

The ratio of TOC percentages to total sulfur (TS) percentages (TOC:TS) in sediments was determined. It ranges from 1.2–3.0 for core SS₁, 0.7–3.0 for MS₁, 0.465–1.226 for MS₂ and 1.2–3.0 for NS₁. Generally, under anoxic conditions dissolved sulfate is reduced to hydrogen sulfide gas, which reacts with iron minerals to form iron sulfides causing a qualitative redox status of the environment under deposition. Marine sediments undergoing sulfate reduction under euxinic/inhospitable bottom conditions typically have TOC:TS ratios lower than 1.5 (Niffy Benny 2009) and similar observation was found at core from

Table 1. Correlation between sedimentary parameters in SS₁ core.

Correlation	Tannin												
	Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-a (mg/kg)	Chl-b (mg/kg)	Chl-c (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Lipid (mg/g)	1.000												
Tannin and lignin (mg/g)	0.503	1.000											
Carbohydrate (mg/g)	-0.241	0.276	1.000										
Protein (mg/g)	-0.036	-0.026	0.446	1.000									
Chl-a (mg/kg)	-0.058	0.529	0.359	0.011	1.000								
Chl-b (mg/kg)	-0.131	0.509	0.233	-0.276	0.805	1.000							
Chl-c (mg/kg)	-0.085	0.474	0.200	-0.292	0.808	0.984	1.000						
Carotenoid (mg/kg)	-0.101	0.440	0.194	-0.284	0.769	0.979	0.993	1.000					
Pheophytin (mg/kg)	0.325	0.571	0.556	0.281	0.637	0.338	0.378	0.335	1.000				
Sand%	0.101	-0.372	-0.521	-0.188	-0.674	-0.370	-0.357	-0.304	-0.773	1.000			
Clay%	-0.119	0.290	0.366	-0.040	0.732	0.489	0.483	0.428	0.708	-0.922	1.000		
Silt%	0.092	0.031	0.142	0.478	-0.457	-0.467	-0.479	-0.449	-0.198	0.270	-0.622	1.000	
BPC%	0.944	0.539	0.028	0.262	0.006	-0.151	-0.114	-0.130	0.478	-0.030	-0.065	0.222	1.000

Table 2. Correlation between sedimentary parameters in MS₁ core.

Correlation	Tannin												
	Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-a (mg/kg)	Chl-b (mg/kg)	Chl-c (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Lipid (mg/g)	1.000												
Tannin and lignin (mg/g)	-0.130	1.000											
Carbohydrate (mg/g)	0.544	0.509	1.000										
Protein (mg/g)	-0.187	-0.302	-0.146	1.000									
Chl-a (mg/kg)	0.311	0.524	0.740	-0.096	1.000								
Chl-b (mg/kg)	0.333	0.328	0.646	-0.119	0.710	1.000							
Chl-c (mg/kg)	0.323	-0.074	0.238	-0.082	0.590	0.448	1.000						
Carotenoid (mg/kg)	0.367	0.479	0.734	-0.058	0.988	0.715	0.548	1.000					
Pheophytin (mg/kg)	0.276	0.584	0.633	-0.025	0.823	0.423	0.238	0.852	1.000				
Sand%	-0.209	-0.504	-0.700	-0.049	-0.834	-0.607	-0.175	-0.861	-0.826	1.000			
Clay%	0.395	0.332	0.719	0.204	0.733	0.628	0.153	0.774	0.656	-0.907	1.000		
Silt%	-0.416	0.418	-0.015	-0.352	0.268	-0.023	0.059	0.237	0.426	-0.257	-0.174	1.000	
BPC%	0.944	0.068	0.779	-0.105	0.509	0.488	0.328	0.552	0.448	-0.430	0.591	-0.352	1.000

Table 3. Correlation between sedimentary parameters in MS₂ core.

Correlation	Tannin												
	Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-a (mg/kg)	Chl-b (mg/kg)	Chl-c (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Lipid (mg/g)	1.000												
Tannin and lignin (mg/g)	0.203	1.000											
Carbohydrate (mg/g)	0.199	0.150	1.000										
Protein (mg/g)	0.306	0.592	0.343	1.000									
Chl-a (mg/kg)	-0.048	0.702	-0.056	0.431	1.000								
Chl-b (mg/kg)	-0.111	0.484	-0.028	0.391	0.798	1.000							
Chl-c (mg/kg)	0.029	0.378	-0.198	0.049	0.660	0.785	1.000						
Carotenoid (mg/kg)	-0.085	0.702	-0.015	0.397	0.973	0.810	0.624	1.000					
Pheophytin (mg/kg)	-0.230	0.303	-0.013	0.259	0.503	0.172	-0.174	0.566	1.000				
Sand%	-0.249	-0.743	-0.116	-0.569	-0.549	-0.392	-0.196	-0.591	-0.378	1.000			
Clay%	0.528	0.506	0.309	0.368	-0.012	-0.166	-0.293	0.076	0.132	-0.568	1.000		
Silt%	-0.033	0.580	-0.055	0.456	0.674	0.582	0.424	0.668	0.374	-0.852	0.053	1.000	
BPC%	0.997	0.228	0.263	0.353	-0.035	-0.095	0.020	-0.069	-0.216	-0.270	0.546	-0.020	1.000

Table 4. Correlation between sedimentary parameters in NS₁ core.

Correlation	Tannin												
	Lipid (mg/g)	Tannin and lignin (mg/g)	Carbohydrate (mg/g)	Protein (mg/g)	Chl-a (mg/kg)	Chl-b (mg/kg)	Chl-c (mg/kg)	Carotenoid (mg/kg)	Pheophytin (mg/kg)	Sand%	Clay%	Silt%	BPC%
Lipid (mg/g)	1.000												
Tannin and lignin (mg/g)	0.668	1.000											
Carbohydrate (mg/g)	0.381	0.716	1.000										
Protein (mg/g)	0.526	0.826	0.750	1.000									
Chl-a (mg/kg)	0.483	0.852	0.618	0.817	1.000								
Chl-b (mg/kg)	-0.001	0.519	0.647	0.498	0.750	1.000							
Chl-c (mg/kg)	0.124	0.548	0.612	0.475	0.728	0.920	1.000						
Carotenoid (mg/kg)	0.240	0.604	0.634	0.613	0.847	0.907	0.912	1.000					
Pheophytin (mg/kg)	0.084	0.566	0.410	0.282	0.406	0.563	0.605	0.478	1.000				
Sand%	-0.638	-0.913	-0.766	-0.880	-0.948	-0.705	-0.697	-0.820	-0.469	1.000			
Clay%	0.668	0.854	0.714	0.843	0.926	0.695	0.714	0.837	0.444	-0.985	1.000		
Silt%	0.096	0.664	0.573	0.541	0.487	0.330	0.189	0.235	0.318	-0.471	0.314	1.000	
BPC%	0.803	0.850	0.855	0.811	0.694	0.423	0.467	0.555	0.310	-0.868	0.850	0.436	1.000

Table 5. *Factor analysis matrix for core SS₁.*

	Component			
	1	2	3	4
Component matrix ^a				
Lipid (mg/g)	-0.018	0.708	0.670	-0.187
Tannin and lignin (mg/g)	0.595	0.505	0.369	0.232
Carbohydrate (mg/g)	0.433	0.318	-0.611	0.335
Protein (mg/g)	-0.104	0.557	-0.583	0.292
Chl- <i>a</i> (mg/kg)	0.932	-0.007	-0.040	0.048
Chl- <i>b</i> (mg/kg)	0.869	-0.303	0.225	0.297
Chl- <i>c</i> (mg/kg)	0.869	-0.290	0.260	0.268
Carotenoid (mg/kg)	0.835	-0.312	0.266	0.316
Pheophytin (mg/kg)	0.716	0.588	-0.168	-0.182
Sand%	-0.734	-0.248	0.465	0.304
Clay%	0.809	0.022	-0.310	-0.484
Silt%	-0.527	0.447	-0.168	0.587
BPC%	0.033	0.879	0.433	-0.064

Extraction method: Principal Component Analysis.

^aFour components extracted.

Table 6. *Factor analysis matrix for core MS₁.*

	Component			
	1	2	3	4
Component matrix ^a				
Lipid (mg/g)	0.507	0.726	0.316	-0.182
Tannin and lignin (mg/g)	0.518	-0.598	0.044	-0.394
Carbohydrate (mg/g)	0.870	0.135	0.045	-0.284
Protein (mg/g)	-0.103	0.218	-0.857	0.321
Chl- <i>a</i> (mg/kg)	0.944	-0.172	0.035	0.232
Chl- <i>b</i> (mg/kg)	0.758	0.086	0.062	0.165
Chl- <i>c</i> (mg/kg)	0.446	0.169	0.392	0.754
Carotenoid (mg/kg)	0.958	-0.123	-0.011	0.207
Pheophytin (mg/kg)	0.837	-0.317	-0.096	-0.047
Sand%	-0.881	0.225	0.307	0.049
Clay%	0.842	0.145	-0.433	-0.096
Silt%	0.127	-0.858	0.275	0.105
BPC%	0.706	0.619	0.177	-0.215

Extraction method: Principal Component Analysis.

^aFour components extracted.

middle zone (MS₂). These sites were under the threat of anthropogenic inputs and were associated with dredging and piling activities. These sediments also undergo sulfate reduction below an oxygenated water column exhibiting TOC:TS ratios in the range 1.5 to 5 and well corroborated earlier by Berner and Raiswell (1983). Sediments in the stations (SS₁, MS₁ and NS₁) were characterized under predominantly anoxic stipulation. Increased anoxia in the study area not only increases preservation of the pigments but also excludes the benthic animal community, thereby reducing ingestion and bioturbation, which has significant effect on the degradation of sedimentary pigments.

C/N ratios are often used to differentiate marine from terrestrial organic matter (Redfield *et al.* 1963; Atkinson and Smith 1983; Perdue and Koprivnjak 2007), although selective degradation of different minerals in sediments can affect the C/N ratios of organic matter (Muller 1997). Organic matter should have a C/N ratio lower than 17 in order to be of nutritional use to invertebrates (Russel Hunter 1970). In this research findings, C/N ratio varied from 18.5 to 25.23, averaging 22.75 for core SS₁; from 11.9 to 14.2, averaging 12.9 for core MS₁; from 20 to 22, averaging 21 for core MS₂ and from 14.4 to 32.8, averaging 20.7 for core NS₁. Among the four cores, C/N ratio

Table 7. Factor analysis matrix for core MS₂.

	Component		
	1	2	3
Component matrix ^a			
Lipid (mg/g)	0.126	0.835	0.432
Tannin and lignin (mg/g)	0.843	0.230	-0.062
Carbohydrate (mg/g)	0.077	0.466	-0.173
Protein (mg/g)	0.633	0.404	-0.138
Chl- <i>a</i> (mg/kg)	0.909	-0.280	0.065
Chl- <i>b</i> (mg/kg)	0.773	-0.374	0.325
Chl- <i>c</i> (mg/kg)	0.566	-0.382	0.695
Carotenoid (mg/kg)	0.917	-0.271	-0.017
Pheophytin (mg/kg)	0.463	-0.157	-0.702
Sand%	-0.814	-0.311	0.218
Clay%	0.267	0.789	-0.268
Silt%	0.818	-0.124	-0.094
BPC%	0.150	0.855	0.407

Extraction method: Principal Component Analysis.

^aThree components extracted.

Table 8. Factor analysis matrix for core NS₁.

	Component		
	1	2	3
Component matrix ^a			
Lipid (mg/g)	0.554	-0.694	-0.357
Tannin and lignin (mg/g)	0.915	-0.250	0.184
Carbohydrate (mg/g)	0.833	-0.050	0.222
Protein (mg/g)	0.862	-0.268	0.086
Chl- <i>a</i> (mg/kg)	0.929	0.042	-0.075
Chl- <i>b</i> (mg/kg)	0.771	0.596	-0.015
Chl- <i>c</i> (mg/kg)	0.774	0.558	-0.172
Carotenoid (mg/kg)	0.848	0.413	0.236
Pheophytin (mg/kg)	0.550	0.399	0.246
Sand%	-0.984	0.101	0.089
Clay%	0.958	-0.081	-0.250
Silt%	0.525	-0.139	0.801
BPC%	0.860	-0.423	-0.052

Extraction method: Principal Component Analysis.

^aThree components extracted.

was greater than 20 in three cores (SS₁, MS₂, and NS₁) ascertaining the input of terrestrial material into the area, justifying that the source of organic matter is allochthonous. From middle zone (core MS₁), the ratio points out autochthonous character of the sediment. However, the succession of post-depositional changes may also modify the environment niche drastically. Percentage of elemental distributions (CHNS) in all the four sediment cores were in the order: C>S>H>N.

To confirm different variable associations, and identification of parameters controlling the organic matter distribution, factor analysis was carried out (tables 5–8). Varimax orthogonal rotation

was employed to transform the analysis matrix and to limit the number of variables loaded in each factor (Buckley *et al.* 1995). In core SS₁, four factors account for 71.3% of the total variance. The first factor accounted for high positive loadings on all the sedimentary parameters except sand, slit and lipid. Factor-2 exhibit significant positive loadings for all OM and BPC. This clearly shows that high negative loading has occurred for all pigments and sand. Factor-3 showed significant positive loading for lipid and high negative loadings for carbohydrate, protein, pigments, clay and slit. Thus it is well established that the third component has undergone geochemical processes rather

than diagenesis, which includes siltation and sorption/desorption. Factor-4 shows no such significant positive loadings. In MS₁ core, four factors account for 84.5% of the total variance. The first factor shows positive loadings of all sedimentary parameters except for sand and protein, evidence to high significant loadings of pigments. Hence, this can be called the 'pigment controlled factor'. High positive loadings of lipid and BPC are the features of factor-2. No such high positive loadings to the sedimentary parameters were found in factor-3, but factor-4 shows significant positive loadings to chl-*c*. In MS₂ core, three factors account for 71.1% of the total variance. The first factor shows positive loadings of all sedimentary parameters except sand and resulting in significant loadings of pigments, and profoundly it could be called the 'pigment controlled factor'. Factor-2 shows high positive loadings on lipid, clay and BPC. But factor-3 shows no such high positive loadings. In core NS₁, three factors account for 69.1% of the total variance. The same trend as in the core MS₂ was observed in the first factor. Though factor-2 shows no such high positive loadings, the factor-3 showed high positive loading to slit. Thus from factor analysis it is inferred that 'organic matter controlled factor', has a maximum amount of total variance in all the four core sediments, indicating good correlation of OM in most of the variables studied. However, combining the sedimentary record with other biological and geochemical indicators in multi-proxy studies still constitutes the most robust method for interpreting long term changes in ecosystem structure.

7. Conclusion

The present study has been the first comprehensive attempt ever made to characterize the core sediment biogeoorganics in the CES. It has served to emphasize the prominent role of biogeoorganics in regulating the complex interactive forces that operate within the estuarine system and also provides a baseline data for future research on anthropogenic impacts in the region. Characterization of organic matter has made it possible to trace the source and predict the fate of allochthonous and autochthonous inputs that find their way into this transition zone. Among the four sediment cores, percentage of TOC was higher at SS₁ and NS₁ coinciding with high clay contents in the southern and northern parts of the estuary. This is attributed to the enhanced adsorption of organic carbon onto the clay minerals in the low salinity regimes. Their relative organic matter distributions in the three cores except NS₁ core were in the order: lipid>carbohydrate>protein>tannin

and lignin. Dominance of carbohydrates over lipids and proteins in the northern zone indicated lower nutritive aspect of the organic matter, and their aged and refractory nature. TOC/TS ratio indicates the anoxic behaviour of all the core sediments. C/N ratio supports the allochthonous character of the three sediment cores (SS₁, NS₁, MS₂). Concentration of pheophytin pigment was found subjugated in three cores (MS₁, MS₂ and NS₁) indicating the long term diagenesis. Increased anoxia in the study area not only increases preservation of pigments, but also excludes the benthic animal community, thereby reducing ingestion and bioturbation, which have a significant effect on the degradation of sedimentary pigments.

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References

- Ahmad M K, Islam S, Rahman S, Haque M R and Islam M M 2010 Heavy metals in water, sediment and some fishes of Buriganga River, Bangladesh; *Int. J. Environ. Res.* **4**(2) 321–332.
- Al-Juboury A I 2009 Natural pollution by some heavy metals in the Tigris River, northern Iraq; *Int. J. Environ. Res.* **3**(2) 189–198.
- Alongi D M 1998 *Coastal Ecosystem Processes*; CRC Press, New York.
- Aneeshkumar N and Sujatha C H 2012 Biomarker pigment signatures in Cochin back water system – a tropical estuary, southwest coast of India; *Estuarine Coast. Shelf Sci.* **99** 182–190.
- APHA 1995 Standard methods for the examination of water and waste water, American Public Health Association, 19th edn, Washington.
- Aspinall G O 1983 *The polysaccharides*, Vol. 2, Academic Press, New York.
- Atkinson M J and Smith S V 1983 C:N:P ratios of benthic marine plants; *Limnol. Oceanogr.* **28** 568–574.
- Barnes H and Blackstock J 1973 Estimation of lipids in marine animals tissues: Detailed investigation of the sulphophosphovanillin method for total lipids; *J. Expt. Mar. Biol. Ecol.* **12** 103–118.
- Berner R and Raiswell R 1983 C/S method for distinguishing fresh water from marine sedimentary rocks; *Geology* **12** 365–368.
- Bianchi T S, Pennock J R and Twilley R R 1999a Biogeochemistry of Gulf of Mexico estuaries: Implications

- for management; In: *Biogeochemistry of Gulf of Mexico Estuaries*, John Wiley, New York, pp. 407–421.
- Biersmith A and Benner R 1998 Carbohydrates in phytoplankton and freshly produced dissolved organic matter; *Mar. Chem.* **63** 131–144.
- Borsheim K Y, Mykkestael S M and Snel J A 1999 Monthly profiles of DOC, mono and polysaccharides at two locations in the Trondheims fjord (Norway) during two years; *Mar. Chem.* **63** 255–272.
- Buckley D E, Smith J N and Winters G V 1995 Accumulation of contaminant metals in marine sediments of Halifax Harbour, Nova Scotia: Environmental factors and historical trends; *Appl. Geochem.* **10**(2) 175–195.
- Burdige D J, Skoog A and Gardener K G 2000 Dissolved and particulate carbohydrate in contrasting marine sediment; *Geochim. Cosmochim. Acta* **64** 1029–1041.
- Chibunda R T, Pereka A E, Phiri E C J and Tungaraza C 2010 Ecotoxicity of mercury contaminated sediment collected from Mabubi River (Geita district, Tanzania) to the early life stages of African Catfish (*Clarias gariepinus*); *Int. J. Environ. Res.* **4**(1) 49–56.
- Cividanes S, Incera M and Lopez J 2002 Temporal variability in the biochemical composition of sedimentary organic matter in an intertidal flat of the Galician coast (NW Spain) ocean; *Acta* **25** 1–12.
- Danovaro R 1996 Detritus–bacteria–meiofauna interactions in a seagrass bed (*Posidonia Oceanica*) of the NW Mediterranean; *Mar. Biol.* **127** 1–13.
- Deepul P M, Gireesh Kumar T R, Sujatha C H and Rejomon George 2011 Chemometric study on the trace metal accumulation in the sediments of the Cochin Estuary – Southwest coast of India; *Environ. Monit. Assess.*, November 2011.
- Dell'Anno A, Pusceddu A and Danovaro R 2002 Assessing the trophic state and eutrophication of coastal marine systems – a new approach based on the biochemical composition of sediment organic matter; *Mar. Pollut. Bull.* **44** 611–622.
- Dubois M, Gilles K A, Hamilton J K, Reebers P A and Smith F 1956 Colorimetric method for the determination of sugars related compounds; *Anal. Chem.* **28** 350–355.
- Fabiano M and Danovaro R 1994 Composition of organic matter in sediments facing a river estuary (Tyrrhenian Sea): Relationships with bacteria and microphytobenthic biomass; *Hydrobiologia* **277** 71–84.
- Fabiano M, Danovaro R and Fraschetti S 1995 Temporal trend analysis of the elemental composition of the sediment organic matter in subtidal sandy sediments of the Ligurian Sea (NW Mediterranean): A three years study; *Cont. Shelf Res.* **15** 1453–1469.
- Fabiano M and Pusceddu A 1998 Total hydrolysable particulate organic matter (carbohydrates, proteins and lipids) at a coastal station in terra Nova Bay (Ross Sea, Antarctica); *Polar Biol.* **19** 125–132.
- Faganelli J, Ogorole B, Misic M, Dollenen T and Pezdic J 1987 Organic geochemistry of two 40 m sediment cores from the Gulf of Trieste Northern Adriatic; *Coast. Shelf Sci.* **25** 157–167.
- Fichez R 1991 Composition and fate of organic matter in submarine cave sediments: Implications for the biogeochemical cycle of organic carbon; *Oceanologica Acta* **14** 369–377.
- Field J A and Lettinga G 1987 The methanogenic toxicity and anaerobic degradability of a hydrolysable tannin; *Water Res.* **21** 367–374.
- Finar I L 1976 Organic Chemistry, Vol. 1, Longman, Singapore.
- Geetha R, Chandramohanakumar N and Mathews L 2008 Geochemical reactivity of surficial and core sediment of a tropical mangrove ecosystem; *Int. J. Environ. Res.* **2**(4) 329–342.
- Gopalan U K, Doyil T, Vengayil P, Udaya V and Krishnankutty M 1983 The shrinking backwaters of Kerala; *J. Mar. Biol. Assoc. India* **25** 131–141.
- Gremare A, Mederach L, Debovee F, Amoroux J M, Vétion G and Albert P 2002 Relationships between sedimentary organics and benthic meiofauna on the continental shelf and the upper slope of the Gulf of Lions (NW Mediterranean); *Mar. Ecol. Prog. Ser.* **234** 85–94.
- Gremare J M, Amouroux, Charles F, Dinét A, Riaux-Gobin C, Baudart J, Medernach L, Bodiou J Y, Vétion G and Colomines J C 1997 Temporal changes in the biochemical composition and nutritional value of the particulate organic matter available to surface deposit feeders: A two-year study; *Mar. Ecol. Prog. Ser.* **150** 195–206.
- Hedges J I and Kiel R G 1995 Sedimentary organic matter preservation: An assessment and speculative synthesis; *Mar. Chem.* **49** 81–115.
- Hobbie J E (ed.) 2000 Estuarine science: The key to progress in coastal ecological research; In: *Estuarine science: A synthetic approach to research and practice*, Island Press, Washington DC, pp. 1–11.
- Holm N G 1988 Arsenic regeneration from estuarine sediments of the Bothnian Bay, Weden; *Chem. Geol.* **68** 89–98.
- Howarth R W, Jaworski N, Swaney D, Townsend A and Billen G 2000 Some approaches for assessing human influences on fluxes of nitrogen and organic carbon to estuaries; In: *Estuarine science: A synthetic approach to research and practice* (ed.) Hobbie J E, Island Press, Washington DC, pp. 17–42.
- Howarth R W, Sharpley A and Walker D 2002 Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals; *Estuaries* **25** 656–676.
- Jose A, Ake C and Vázquez G 2008 Phytoplankton variation and its relation to nutrients and allochthonous organic matter in a coastal lagoon on the Gulf of Mexico; *Estuarine Coast. Shelf Sci.* **78** 705–714.
- Karbassi A R and Shankar R 2005 Geochemistry of two sediment cores from the west coast of India; *Int. J. Environ. Sci. Tech.* **1**(4) 307–316.
- Lewis D W 1984 *Practical sedimentology*; Hutchinson Ross Publishing Co., Stroudsburg, 229p.
- Lowry O H, Rosebrough N J, Farr A L and Randall R J 1951 Protein measurement with Folin Phenol reagent; *J. Biol. Chem.* **193** 265–275.
- Manju Mary Joseph, Ratheesh Kumar C S, Gireesh Kumar T R, Renjith K R and Chandramohanakumar N 2008 Biogeochemistry of surficial sediments in the intertidal systems of a tropical environment; *Chem. Ecol.* **24** 247–258.
- Menon N, Balachand N and Menon A N 2000 Hydrobiology of the Cochin backwater system – A review; *Hydrobiologia* **430** 149–183.
- Middelburg Jack J, Gerard K, Joop N, Annette W, Hass Wim De, Tom V, Jaco F W A and Van der N 1996 Organic matter mineralization in intertidal sediments along an estuarine gradient; *Marine Ecol. Progr. Series* **132** 157–168.
- Muller P J 1997 C/N ratios in Pacific deep sea sediments: Effect of inorganic ammonium and organic nitrogen compound sorbed by clays; *Geochim. Cosmochim. Acta* **41** 765–776.
- Niffy Benny 2009 Unravelling a benchmark for sulphur akin in the Cochin Estuarine System; Ph.D Thesis,

- Cochin University of Science and Technology, Cochin, Kerala.
- Parsons T R, Takahashi M and Hargrave B 1984 *Biological Oceanographic Processes*; 3rd edn, Pergamon Press, New York.
- Perdue E M and Koprivnjak J F 2007 Using the C/N ratio to estimate terrigenous inputs of organic matter to aquatic environments; *Estuarine Coast. Shelf Sci.* **73** 65–72.
- Redfield A C, Ketchum B H and Richards F A 1963 The influence of organisms on the composition of sea-water; In: *In the Sea* (ed.) Hill N, 2nd edn, Wiley, New York, pp. 26–77.
- Rich J H, Decklow H W and Kirchman D L 1996 Concentration and uptake of neutral monosaccharides along 140°W in the equatorial pacific: Contribution of glucose to heterotrophic bacterial activity and DOM flux; *Limnol. Oceanogr.* **41** 595–604.
- Russel Hunter W D 1970 *Aquatic productivity: An introduction to some basic aspects of biological oceanography and limnology*; Collier-Macmillan, London, 306p.
- Schnitzer M and Khan S U 1972 *Humic substances in the environment*; Marcel Dekker, New York, 327p.
- Skoog A and Benner R 1997 Dldose in various size fractions of marine organic matter: Implications for carbon cycling; *Limnol. Oceanogr.* **42(8)** 1803–1813.

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