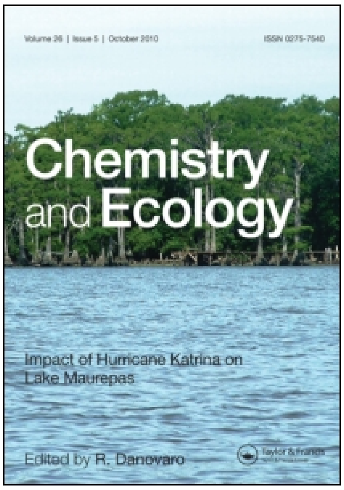

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Biogeochemistry of surficial sediments in the intertidal systems of a tropical environment

Manju Mary Joseph[a]; C.S. Ratheesh Kumar[a]; T.R. Gireesh Kumar[a]; K. R. Renjith[a]; N. Chandramohanakumar[a]
[a] Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi, Kerala, India

To cite this Article Joseph, Manju Mary , Kumar, C.S. Ratheesh , Kumar, T.R. Gireesh , Renjith, K. R. and Chandramohanakumar, N.(2008) 'Biogeochemistry of surficial sediments in the intertidal systems of a tropical environment', Chemistry and Ecology, 24: 4, 247 — 258

To link to this Article: DOI: 10.1080/02757540802119871

URL: http://dx.doi.org/10.1080/02757540802119871

Chemistry and Ecology
Vol. 24, No. 4, August 2008, 247–258

Biogeochemistry of surficial sediments in the intertidal systems of a tropical environment

Manju Mary Joseph*, C.S. Ratheesh Kumar, T.R. Gireesh Kumar, K.R. Renjith and N. Chandramohanakumar

Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi, Kerala, India

(*Received 19 January 2008; final version received 25 March 2008*)

Variability of nature and composition of organic matter in the surficial sediments of mangrove and estuarine systems of Cochin were investigated. Assessment of biochemical composition and elements such as carbon, nitrogen and sulphur were employed for this. Irrespective of the higher content of total organic matter, the labile organic matter was very low in both mangrove and estuarine sediments. Concentrations of biochemical compounds were comparatively higher in mangrove sediments. Total lipids were the dominant class among labile organic compounds in both mangrove and estuarine sediments contributing 51.4% and 45.3%, respectively. Protein to carbohydrate ratio was higher in estuarine sediments when compared to mangroves, indicating low dead organic matter accumulation, probably due to the strong hydrodynamic conditions in estuaries. Correlation analysis showed that sediment texture had no significant correlation with any of the sedimentary parameters in mangroves, whereas in estuaries, it showed significant correlations with most of the sedimentary parameters. Principal component analysis indicated three different dominant processes in mangroves namely mangrove litter addition, diagenesis and other geochemical process like siltation and sorption/desorption, while in estuaries the dominant process seems to be diagenesis.

Keywords: biochemical composition; tropical estuary; mangrove; lipids; proteins; carbohydrates

1. Introduction

Coastal ecosystems are widely recognised as biogeochemically active regions, where organic matter inputs from a variety of sources undergo intense biogeochemical processing. Organic matter in marine sediments is composed of labile and refractory compounds, whose relative importance changes as a function of a complex array of processes, including degradation, heterotrophic utilisation, transformation, accumulation and export [1]. Refractory organic compounds such as humic and fulvic acids, structural carbohydrates and 'black' carbon account generally for most of the sedimentary organic matter and are easily accumulated in marine sediments [2,3]. Conversely, the labile fraction of organic matter consists mainly of simple and/or combined molecules (i.e. biopolymers); it includes carbohydrates, lipids and proteins, which are assumed to represent the fraction of organic matter more readily available to benthic consumers [4,5]. Quantity and quality

*Corresponding author. Email: manjumaryjoseph@yahoo.co.in

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540802119871
http://www.informaworld.com

of organic matter in surface sediments are considered to be major factors affecting benthic fauna dynamics and metabolism [6,7]. This is accomplished with the use of biochemical indices like concentrations of protein, carbohydrate, lipids, protein/carbohydrate ratio and lipid/carbohydrate ratio [8,9]. The labile portion of organic matter could also be suitable to assess the trophic status of coastal marine systems [5,10].

However, there is a conspicuous lack of information about concentrations and variability of these compounds in intertidal sediments. Due to their dynamic ecotonal location, these environments display strong spatial and temporal variability of major biogeochemical characteristics. The biogeochemical properties of mangroves are the least understood ecological properties because of their sediment complexity due to the tidal influx of allochthonous organic matter and also the input of local vegetation. The present study compares biochemical composition of organic materials in the sediments of two different intertidal ecosystems of Cochin, southwest coast of India. The main objective of the study was to investigate the quantity and quality of organic matter in the surficial sediments of these ecosystems and thereby to identify the major biogeochemical pathways.

2. Materials and methods

2.1. *Study area*

Cochin estuary, the largest estuarine system in the southwest coast of India, is a part of the Vembanad-Kol wetlands (09°50’N, 76°45’E), which is a Ramsar Site (No.1214). This estuary is topographically divisible into two arms; a southern one extending south of barmouth from Cochin to Thanneermukkam and a northern one extending north from Cochin to Azhikode. This tropical aquatic system is under the profound influence of the monsoon, which contributes to about 71% of the annual rainfall [11] and accordingly there are three seasonal conditions prevailing viz. monsoon (June–September), post-monsoon (October–January) and pre-monsoon (February–May). Tides at Cochin are of a mixed semi-diurnal type, with the maximum spring tide range of about 1 m [12], resulting in incomplete flushing. The abundant mangrove vegetation of these regions has been shrinking in area due to land reclamation and developmental activities and also due to pollution by industrial effluents as well as domestic sewage.

Three mangrove systems and three estuarine stations along the northern arm were chosen for the present study (Figure 1). Among the mangrove locations, Station 1 (M1), Puthuvyppu, is a mangrove nursery maintained by the fisheries research unit of Kerala Agricultural University, located about 200 m away from the estuarine front and is free from sewage inputs. Station 2 (M2), Murikkumpadam, is a densely populated fishermen-settlement. The discharge of sewage and disposal of garbage and solid waste add to the problem of pollution. These stations form part of the island called Vypin, which is one of the most densely populated coastal zones. Station 3 (M3), Manglavanam, is a patchy mangrove area in the heart of the city of Cochin. This mangrove forest is a small bird sanctuary, as well. It is the home of many exotic and rare varieties of migratory birds. This is an almost closed system with a single narrow canal linking to the estuary, which is the only source for tidal propagation. All the estuarine stations (E1, E2 and E3) selected are adjacent to these mangrove ecosystems.

2.2. *Sampling and analytical methodology*

Samples of water and sediments were taken from these locations during December 2005, April 2006 and July 2006 representing the post-monsoon, pre-monsoon and monsoon seasons, respectively. Surface water samples were taken using a clean plastic bucket. A Van Veen grab (0.042 m^2)

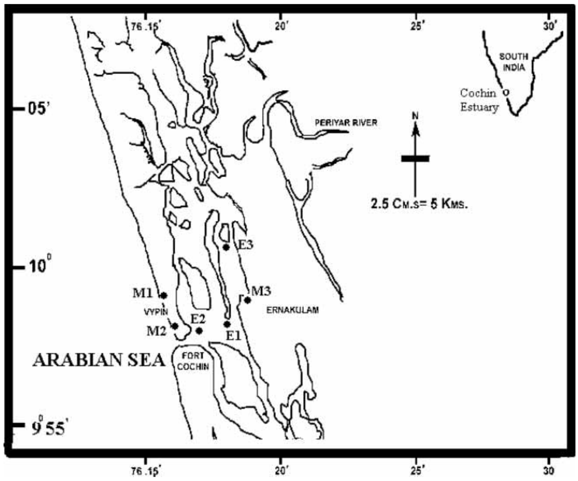

Figure 1. Study region. M and E represent the mangrove and estuarine stations, respectively.

and a clean plastic spoon were used for collecting surficial sediments. Samples were transported to the lab on ice and stored in a deep freezer.

pH in the water column was measured *in situ* and temperature was measured using a sensitive thermometer. Salinity of the water samples was estimated by the Mohr-Knudsen method [13]. A modified Winkler method was used for the estimation of dissolved oxygen [14]. Alkalinity of the water samples was estimated by the method of Koroleff, using Bromothymol blue as the indicator [15].

Textural analysis of the sediment was done based on Stoke's law using the method of Krumbein and Pettijohn [16]. Sediment samples were air dried and finely powdered using agate mortar for the further analyses. Total carbon, nitrogen and sulphur were determined using a Vario EL III CHNS Analyzer. Sediment organic carbon was estimated on dried sediments by the procedure of El Wakeel and Riley modified by Gaudette and Flight [17]. The amount of total organic matter (TOM) was obtained by multiplying the organic carbon values with 1.724 [18]. Colorimetric methods were employed for determination of biochemical compounds. Protein (PRT) analyses were carried out following the procedure of Lowry et al. [19], as modified by Rice [20] to account for the reactivity of phenolic compounds, with albumin as standard. The amount of protein nitrogen was obtained by multiplying protein with 0.16 [21]. Total carbohydrates (CHO) were analysed according to Dubois et al. [22], using glucose as standard. Total lipids (LPD) were extracted according to Bligh and Dyer [23], and estimated according to Barnes and Blackstock [24] using cholesterol as standard. All analyses were carried out in triplicate and the average is reported. The sum of all proteins, carbohydrates and lipids was defined as labile or easily assimilable organic fraction [25,26]. 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 [27]. The sum of protein, carbohydrate and lipid carbon was referred as biopolymeric carbon (BPC) [4,28].

3. Results

3.1. *General hydrographic condition*

The southwest monsoon was found to have great influence on the study region, creating significant seasonal variations in the hydrographical parameters. Salinity varied widely in this aquatic system and near freshwater conditions seen during the monsoon season were gradually transformed to a marine condition during pre-monsoon. It ranged between 1.3 and 34.03 psu and between 0.04 and 33.02 psu, respectively in mangrove and estuarine stations. pH in mangroves varied from 6.6 to 7.6 whereas in estuarine stations it was slightly more alkaline, ranging between 7.01 and 8.8. Alkalinity in mangroves varied from 68 to 216 mg CaCO3/l and for estuarine stations the range was from 18 to 317 mg CaCO3/l. Dissolved oxygen content in mangroves ranged from 1.4 to 6.4 mg O2/l, while in estuary a narrow range of 4.9 to 8 mg O2/l was observed.

3.2. *General sediment characteristics*

Results of the sedimentary analysis of mangroves and estuarine stations are presented in Tables 1 and 2, respectively. Texture analysis showed that in the mangrove sediments, silt was found to be the major fraction while in estuary, it varied. Station 1 is silty in nature; station 2 is sandy and station 3 is clayey in nature. Total carbon content in mangrove stations ranged between 2.91 and 7.64% dry weight, whereas in estuary it varied between 0.47 and 3.04% dry weight. Total organic carbons content in mangroves ranged from 2.2 to 6.7% dry weight and in estuary it varied from 0.22 to 2.76% dry weight. Total organic matter content ranged from 3.8 to 11.6% dry weight and from 0.38 to 4.8% dry weight in mangrove and estuarine sediments. Total nitrogen content ranged from 0.27 to 0.66% and from 0.02 to 0.3% dry weight respectively in mangrove and estuarine sediments. Total sulphur in mangroves ranged between 0.22 and 1.96% dry weight and in estuarine stations it ranged between 0.18 and 1.70% dry weight.

3.3. *Biochemical composition of sedimentary organic matter*

Protein concentrations ranged from 702–4608 μg/g and from 205–1924 μg/g in mangrove and estuarine sediments, respectively. The protein nitrogen concentrations for mangrove and estuarine sediments varied from 112–737 μg/g and from 33–308 μg/g, respectively. The ranges for total carbohydrates at these stations were 505–2458 μg/g, and 250–1229 μg/g, respectively. Total lipids ranged from 804–6816 μg/g in mangroves and from 312–2815 μg/g at estuarine sediments. The biochemical composition was higher in mangrove sediments than in estuarine sediments. The biopolymeric carbon fraction of sedimentary organic carbon in mangroves ranged from 1291–8057 μg C/g and in estuary from 466–3056 μg C/g.

Analysis of variance showed that sediment texture did not have any significant seasonal variations in two ecosystems, while in estuarine stations a significant spatial variation was observed. Carbon and nitrogen showed no significant variations in mangroves, while sulphur was significantly higher at M3. Similar variations were observed for estuaries also. Lipids showed significant spatial variations with higher values at M3, while protein did not show any variations. Carbohydrates showed significantly higher values during post-monsoon season in mangroves. Lipids showed significant spatial variations in estuarine stations, while protein showed significant spatial and temporal variations. Spatial as well as temporal variations were absent for carbohydrate in the estuarine ecosystem. BPC showed no significant variations in mangroves, while a spatial variation was noticed for estuarine stations.

4. Discussion

Irrespective of the higher content of total organic matter (TOM), the labile organic matter (LOM) was very low in both mangrove and estuarine sediments. The contribution of labile organic matter

Table 1. Seasonal variations of sedimentary parameters in the surficial sediments of mangrove ecosystems. Results of ANOVA are also shown.

	M1			M2			M3			ANOVA P-value	
Parameters	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post	Spatial	Seasonal
Sand (%)	6.73 ± 1.9	36.60 ± 4.8	8.87 ± 2.86	4.34 ± 1.1	2.32 ± 0.91	0.94 ± 0.09	23.59 ± 2.6	–	10.46 ± 1.92	0.115	0.16
Silt (%)	71.79 ± 6.8	28.51 ± 3.0	58.92 ± 4.17	59.97 ± 2.1	63.78 ± 6.7	59.38 ± 6.9	45.56 ± 3.1	–	70.47 ± 5.7	0.786	0.428
Clay (%)	21.45 ± 2.21	34.89 ± 2.69	32.20 ± 2.32	35.69 ± 2.71	33.90 ± 2.78	39.68 ± 2.79	21.97 ± 3.1	–	19.07 ± 2.22	0.069	0.62
Total carbon (%)	3.73 ± 0.11	6.75 ± 0.07	4.72 ± 0.04	2.91 ± 0.06	3.31 ± 0.05	6.25 ± 0.11	5.52 ± 0.09	–	7.64 ± 0.09	0.205	0.233
Organic carbon (%)	2.8 ± 0.01	6.3 ± 0.13	3.9 ± 0.03	2.2 ± 0.02	2.5 ± 0.03	4.9 ± 0.05	5 ± 0.06	–	6.7 ± 0.13	0.145	0.276
Total nitrogen (%)	0.34 ± 0.07	0.50 ± 0.01	0.32 ± 0.01	0.27 ± 0.05	0.29 ± 0.006	0.46 ± 0.009	0.47 ± 0.01	–	0.66 ± 0.01	0.104	0.385
Total sulphur (%)	0.32 ± 0.006	0.25 ± 0.005	0.62 ± 0.1	0.35 ± 0.012	0.22 ± 0.004	0.63 ± 0.013	1.96 ± 0.02	–	1.14 ± 0.023	0.022	0.603
Total lipids (μg/g)	2789 ± 155.8	2360 ± 47.2	2244 ± 102.4	1534 ± 23.01	804 ± 34.5	1620 ± 86.2	5931 ± 359.3	–	6816 ± 602.2	0.0003	0.48
Protein (μg/g)	887 ± 13.3	1400 ± 25.2	1527 ± 16.8	702 ± 8.4	870 ± 13.05	1325 ± 13.25	887 ± 14.2	–	4608 ± 17.7	0.228	0.204
Total carbohydrates (μg/g)	1043 ± 12.5	779 ± 9.3	1790 ± 23.3	1000 ± 34	653 ± 8.5	2458 ± 49.2	505 ± 10.1	–	1716 ± 68.64	0.284	0.007
BPC (μg/g)	2944	2767	3147	1895	1291	2848	5085	–	8057	0.115	0.16
C/N Ratio	8.24	12.6	12.19	8.15	8.62	10.65	10.64	–	10.15		
PRT/CHO	0.85	1.8	0.85	0.7	1.34	0.54	1.76	–	2.68		
LPD/CHO	2.68	3.03	1.25	1.53	1.23	0.66	11.74	–	3.97		

Note: Pre, Pre-monsoon; Mon, Monsoon; Post, Post-monsoon.

Table 2. Seasonal variations of sedimentary parameters in the surficial sediments of estuary. Results of ANOVA are also shown.

	M1			M2			M3			ANOVA P-value	
Parameters	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post	Spatial	Seasonal
Sand (%)	10.64 ± 0.91	9.65 ± 0.93	13.50 ± 1.27	73.68 ± 2.47	75.93 ± 2.52	87.69 ± 4.75	61.44 ± 2.84	70.3 ± 2.27	17.18 ± 0.21	0.031	0.732
Silt (%)	61.47 ± 2.11	57.75 ± 1.73	48.63 ± 0.9	9.90 ± 0.2	16.56 ± 0.66	4.07 ± 0.08	27.23 ± 0.54	21.4 ± 0.43	45.55 ± 0.82	0.018	0.993
Clay (%)	27.90 ± 0.56	32.59 ± 0.65	37.87 ± 1.28	16.42 ± 0.81	7.51 ± 0.15	8.24 ± 0.17	11.34 ± 0.22	8.32 ± 0.36	37.27 ± 0.77	0.113	0.391
Total carbon (%)	2.90 ± 0.58	3 ± 0.06	3.04 ± 0.06	0.47 ± 0.03	1.32 ± 0.05	0.83 ± 0.07	0.98 ± 0.05	0.54 ± 0.09	2.85 ± 0.5	0.062	0.481
Organic carbon (%)	2.76 ± 0.11	1.9 ± 0.1	2.75 ± 0.13	0.22 ± 0.06	0.96 ± 0.04	0.54 ± 0.01	0.45 ± 0.005	0.24 ± 0.006	2.3 ± 0.08	0.069	0.402
Total nitrogen (%)	0.26 ± 0.04	0.3 ± 0.008	0.27 ± 0.01	0.02 ± 0.009	0.13 ± 0.06	0.04 ± 0.003	0.05 ± 0.001	0.05 ± 0.007	0.27 ± 0.02	0.083	0.542
Total sulphur (%)	1.70 ± 0.1	1.48 ± 0.2	1.50 ± 0.5	0.18 ± 0.01	0.57 ± 0.004	0.25 ± 0.02	0.76 ± 0.09	0.29 ± 0.002	1.41 ± 0.09	0.047	0.717
Total lipids (μg/g)	2375 ± 210	2815 ± 256	2326 ± 178	312 ± 48	1255 ± 24	595 ± 64	698 ± 13	719 ± 24	1539 ± 124	0.013	0.442
Protein (μg/g)	1724 ± 264	1025 ± 14	1924 ± 102	270 ± 36	331 ± 16	694 ± 24	673 ± 51	205 ± 13	1252 ± 128	0.009	0.037
Total carbohydrates (μg/g)	1013 ± 136	594 ± 74	923 ± 38	250 ± 12	1229 ± 76	250 ± 18	513 ± 12	351 ± 63	1171 ± 141	0.822	0.901
BPC (μg/g)	3031	2851	3056	466	1595	886	1058	780	2237	0.03	0.582
C/N ratio	10.62	6.3	10.19	11	7.38	13.5	9	4.8	8.52		
PRT/CHO	1.7	1.72	2.08	1.08	0.27	2.77	1.31	0.58	1.07		
LPD/CHO	2.34	4.74	2.52	1.25	1.02	2.38	1.36	2.05	1.31		

Note: Pre, Pre-monsoon; Mon, Monsoon; Post, Post-monsoon.

to total organic matter pool in mangrove sediments ranged from 4.16–11.45% whereas in estuarine sediments it ranged from 9.43–31.10%. Hence in both sediments a large fraction of total organic matter is represented by refractory material or is uncharacterised. The refractory fraction was comparatively higher in mangrove sediments.

Total nitrogen concentrations of mangrove sediments were higher than that of estuarine sediments. Labile nitrogen, which is widely considered as the major limiting factor for deposit-feeders was 5.94% of the total nitrogen in mangrove sediments and 12.94% in estuarine sediments. Hence sedimentary nitrogen was more refractory in mangroves than in estuaries. Nitrogen occurring in sedimentary organic matter (SOM) mainly derives from living organisms. Proteins and peptides, the most abundant nitrogen containing substances in SOM, have been traditionally considered part of the labile fraction in the environment, although recent studies have shown that proteinaceous material can resist microbial degradation in sedimentary environments and consequently a portion of the nitrogen is incorporated into biologically refractory organic material and removed from the active nitrogen pool [29–31]. Thus although the large amount of organic matter was present in Cochin mangrove sediments, this detritus was of relatively low nutritional quality.

Stoichiometric ratios of nutrients are utilised to determine the origin and transformation of organic matter based on the generalisation that organic matter derived from marine plankton has atomic C/N ratios between 4 and 10 while mangrove plants have C/N ratios of 20 and above [32–34]. However the selective degradation of the different minerals in sediments can affect the C/N ratios of organic matter [35]. In shallow coastal ecosystems, most of the organic carbon and nitrogen produced by microphytobenthos and macroalgae rather than phytoplankton [36, 37]. Organic matter should have a C/N ratio lower than 17 in order to be of nutritional use to invertebrates [38]. The C/N ratios in mangroves ranged from 8.15–12.6 and in estuaries it varied between 4.8 and 13.5, which are comparable with similar aquatic environments [39].

Protein to carbohydrate ratio (PRT: CHO) is used as an index to determine the origin of material present in sediments and to determine the age of sedimentary organic matter [25,26]. Since bacteria use proteins more readily than carbohydrates [40], high PRT:CHO ratios indicate living organic matter or newly generated detritus [25]. On the other hand, low PRT:CHO ratios suggest the presence of aged organic matter [25] and the role of proteins as a potentially limiting factor for benthic consumers [4]. This ratio ranges from lower than 0.1 in oligotrophic deep-sea sediments (500–2400 m depth in the Eastern Mediterranean Sea [25]) to higher than 10 in coastal Antarctic sediments [41]. Values of the protein to carbohydrate ratio greater than 1 are associated generally with recently produced organic matter; typically they are reported immediately after a microphytobenthic bloom [4] or after the deposition of freshly produced phytoplankton [42].

The PRT:CHO ratio was generally higher in estuarine sediments than in mangrove sediments. Estuaries are generally subjected to strong hydrodynamic conditions such as tidal action, mixing and freshwater discharge and hence it is more dynamic compared to mangroves, where there is very low water exchange. The higher PRT:CHO ratios in estuarine sediments when compared to mangroves indicated that in the former there is low dead organic matter accumulation, probably due to the strong hydrodynamic condition of estuaries. On the contrary, the low hydrodynamic condition in mangroves favours the accumulation of sedimentary organic matter. The source organic matter character of the mangrove sediments may also be contributing to this lower ratio.

The lipid content and lipid to carbohydrate ratio (LPD:CHO) have been used as good indices to describe the energetic (food) quality of the organic contents in the sediments [9,43,44]. Furthermore, lipid concentrations have been associated with the most labile fraction of sedimentary organics and it is considered as the best descriptor for meiofauna abundance and biomass over enzymatically hydrolysable amino acids or protein contents [9,43,45]. LPD:CHO ratio ranged from 0.66–11.74 in mangroves and in estuary it ranged from 1.02–4.74. The mangrove sediments showed higher concentrations of lipids and consequently high LPD:CHO ratio than that

Table 3. Correlation between sedimentary parameters in the mangrove ecosystem ($n = 8$).

	Sand	Silt	Clay	Total carbon	Organic carbon	Total nitrogen	Total sulphur	Total lipids	Protein	Total carbohydrates	BPC
Sand	1										
Silt	−0.86	1									
Clay	−0.16	−0.32	1								
Total carbon	0.48	−0.32	−0.22	1							
Organic carbon	0.61	−0.43	−0.25	0.99	1						
Total nitrogen	0.43	−0.17	−0.43	0.95	0.94	1					
Total sulphur	0.26	−0.10	−0.57	0.42	0.44	0.51	1				
Total lipids	0.344	0.042	−0.83	0.61	0.64	0.77	0.82	1			
Protein	0.14	0.19	−0.59	0.75	0.74	0.86	0.52	0.83	1		
Carbohydrates	−0.47	0.36	0.26	0.39	0.25	0.26	−0.07	−0.04	0.29	1	
BPC	0.21	0.16	−0.74	0.72	0.72	0.85	0.68	0.95	0.95	0.21	1

of estuarine sediments. Mangroves are generally considered as promoters of estuarine production. The high LPD:CHO ratio, which is an index of energy character, supports the above statement.

Correlation analysis of mangrove sediments (Table 3) showed that BPC had highly significant positive relations with total nitrogen, total lipids and proteins, while significant correlations were obtained with total carbon and organic carbon contents. Total lipids showed highly significant positive correlations with total sulphur and significant correlations with total nitrogen and protein. Proteins also showed significant positive correlations with total carbon and organic carbon. Texture had no significant positive correlation with any of the parameters in the mangrove sediments. Total carbohydrates were also not correlated with any sedimentary parameters. But a clear difference was noticed in estuary, where all biochemical parameters except carbohydrates showed significant positive correlation with texture, total carbon, organic carbon, total nitrogen and total sulphur (Table 4). Total carbohydrates showed significant positive correlations of with organic carbon and total nitrogen in estuary.

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

Table 4. Correlation between sedimentary parameters in estuary ($n = 9$).

	Sand	Silt	Clay	Total carbon	Organic carbon	Total nitrogen	Total sulphur	Total lipids	Protein	Total carbohydrates	BPC
Sand	1										
Silt	−0.98	1									
Clay	−0.93	0.84	1								
Total carbon	−0.95	0.92	0.91	1							
Organic carbon	−0.92	0.88	0.88	0.97	1						
Total nitrogen	−0.94	0.91	0.89	0.99	0.95	1					
Total sulphur	−0.97	0.97	0.87	0.97	0.95	0.95	1				
Total lipids	−0.90	0.91	0.77	0.93	0.88	0.95	0.91	1			
Protein	−0.85	0.80	0.83	0.88	0.94	0.81	0.89	0.77	1		
Carbohydrates	−0.53	0.53	0.47	0.66	0.70	0.68	0.65	0.55	0.51	1	
BPC	−0.92	0.92	0.83	0.98	0.96	0.97	0.96	0.97	0.88	0.66	1

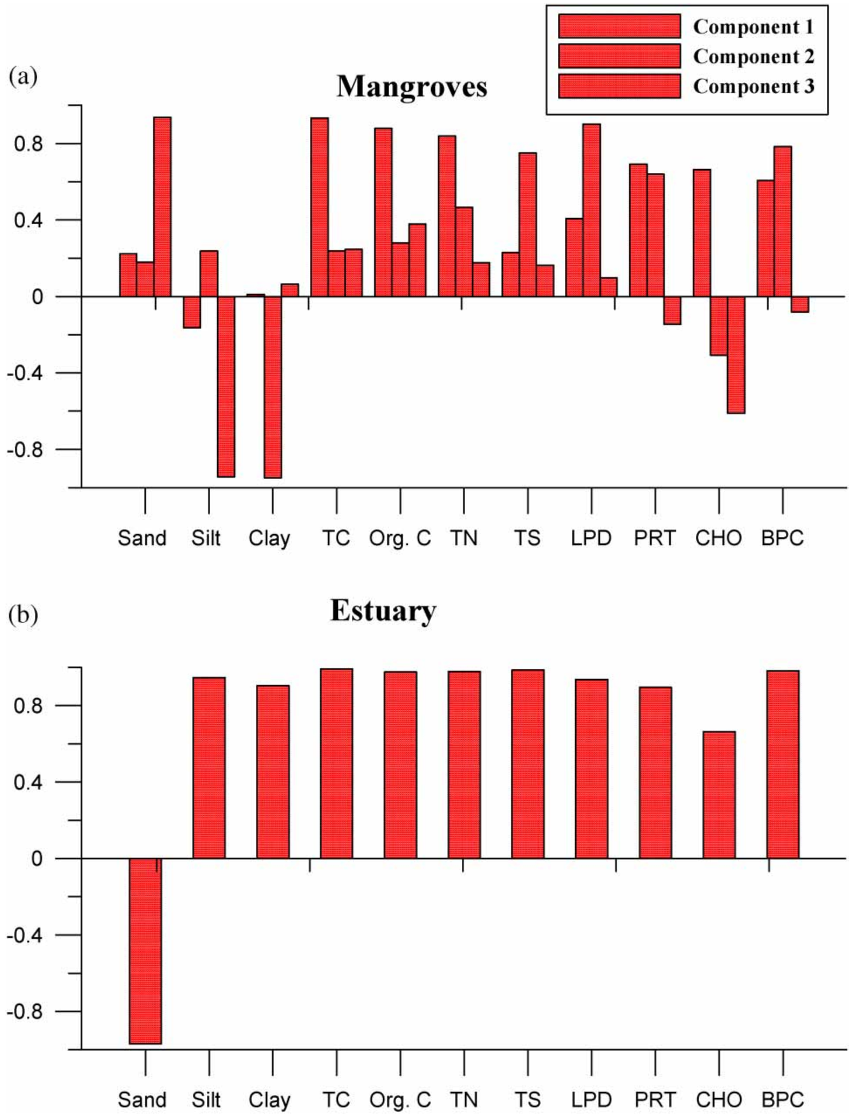

Figure 2. Loading pattern of various biogeochemical parameters for the different components in PCA analysis of (a) mangrove and (b) estuarine systems.

The possible biogeochemical processes that can operate on the organic matter in aquatic systems are the diagenesis, allochthonous and autochthonous additions and sorption/desorption. Diagenesis is a redox process, largely mediated by sedimentary microorganisms and the suitable indicators to this are the redox element sulphur, organic carbon and nitrogen. The relation of sedimentary parameters with grain size can give indication about the sorption/desorption processes.

PCA analysis of estuarine sediments gives only one component accounting for 89.37% variance (Figure 2a). It shows high positive loadings on all the sedimentary parameters except sand, which shows high negative loading. The high positive loadings for redox indicators such as total sulphur, total and organic carbon and total nitrogen indicate that the major process that can operate in the system is the diagenesis.

PCA analysis of mangrove sediments shows that three components without significant differences account for a total of 92.84% variance (Figure 2b). First component accounts for 35.77% of the total variance and shows very high positive loadings on biochemical compounds (except lipids), total carbon, organic carbon, total nitrogen and BPC. But this component has no significant loadings on sediment texture and total sulphur, one of the major redox indicators. Hence the first factor seems to be mangrove litter addition and this could be the main source of organic matter in mangrove sediments.

Component 2 shows high negative loadings on clay and positive loadings on sulphur, lipids and BPC accounts for 34.84% of total variance. It also has a statistically significant negative loading on carbohydrate, which points towards the diagenetic pathway. The low negative loading pattern for carbohydrates might be due to the preferential remineralisation of lipids and proteins. It is established that carbohydrates are diagenetically weaker than proteins under anoxic conditions, but the reverse is true under oxic conditions [46]. Thus the anaerobic diagenetic processes account for the second major geochemical processes in these ecosystems.

Component 3 accounts for 22.23% of total variance and shows high positive loadings on sand and negative loadings on silt and carbohydrates. Also from the positive loadings on organic carbon and low loading on clay it seems that third component is the geochemical processes other than diagenesis, which includes siltation and sorption/desorption.

5. Conclusion

Sedimentary organic matter is higher in mangroves than in their adjoining estuary. However the percentage ratio of the labile to total organic matter indicated that most of the deposited organic matter is refractory in both environments. The refractory fraction was higher in mangrove sediments when compared to estuarine sediments. This discrepancy between the high amounts of organic matter and its low nutritional value suggests that these ecosystems behave as a detrital trap and organic matter tends to accumulate. Statistical analysis revealed the difference in biochemical characteristics of these two ecosystems and showed that the biogeochemistry of mangrove sediments is very complex and cannot be explained effectively by using elemental ratios or biochemical composition. Further studies like biomarker and stable isotopic analysis are essential to understand the origin and fate of the large detrital pool in these sediments.

Acknowledgements

The authors gratefully acknowledge the facilities and the support provided by the Director, School of Marine Sciences and the Dean, Faculty of Marine Sciences, Cochin University of Science and Technology.

References

[1] E. Viollier, C. Rabouille, S.E. Apitz, E. Breuerd, G. Chaillou, K. Dedieub, Y. Furukawaf, C. Grenz, P. Hall, and F. Janssen, *Benthic biogeochemistry: State of the art technologies and guidelines for the future of in situ survey*, J. Exp. Mar. Biol. Ecol. 285–286 (2003), pp. 5–31.

[2] J.J. Middelburg, J. Nieuwenhuize, and P. van-Breugel, *Black carbon in marine sediments*, Mar. Chem. 65 (1999), pp. 245–252.

[3] Y. Zegouagh, S. Derenne, C. Largeau, P. Bertrand, M.A. Sicre, A. Saliot, and B. Rousseau, *Refractory organic matter in sediments from the Northwest African upwelling system: Abundance, chemical structure and origin*, Organic Geochem. 30 (1999), pp. 101–117.

[4] M. Fabiano, R. Danovaro, and S. Fraschetti, *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 (1995), pp. 1453–1469.

[5] A. Dell'Anno, M.L. Mei, A. Pusceddu, and R. Danovaro, *Assessing the thropic state and eutrophication of coastal marine systems. A new approach based on the biochemical composition of sediment organic matter*, Mar. Poll. Bull. 44 (2002), pp. 611–622.

[6] T. Graf, R. Shulz, R. Peinert, and L.A. Meyer-Reil, *Benthos response to sedimentation during autumn to spring at a shallow water station in the western Kiel bight. I. Analysis of the processes on the community level*, Mar. Biol. 77 (1983), pp. 235–246.

[7] J. Grant and B.T. Hargrave, *Benthic metabolism and the quality of sediment organic carbon*, Biol. Oceanogr. 4 (1987), pp. 243–264.

[8] A. Dell'Anno, M. Fabiano, M.L. Mei, and R. Danovaro, *Enzymatically hydrolysed protein and carbohydrate pools in deep-sea sediments: Estimates of the potentially bioavailable fraction and methodological considerations*, Mar. Ecol. Prog. Ser. 196 (2000), pp. 15–23.

[9] A. Grémare, L. Medernach, F. deBovée, J.M. Amoroux, G. Vétion, and P. Albert, *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 (2002), pp. 85–94.

[10] A. Pusceddu, A. Dell'Anno, R. Danovaro, E. Manini, G. Sarà, and M. Fabiano, *Enzymatically hydrolyzable protein and carbohydrate sedimentary pools as indicators of the trophic state of detritus sink systems: A case study in the Mediterranean coastal lagoon*, Estuaries 26 (2003), pp. 641–650.

[11] A.A. Jayaprakash, *Long term trends in rainfall, sea level and solar periodicity: A case study for forecast of Malabar sole and Oil sardine fishery*, J. Mar. Biol. Ass. India 44 (2002), pp. 163–175.

[12] K. Srinivas, *Seasonal and interannual variability of sea level and associated surface meteorological parameters at Cochin*, PhD Thesis, Cochin University of Science and Technology, Cochin, India, 1999.

[13] T.J. Muller, *Determination of salinity*, in *Methods of Sea Water Analyses*, K. Grasshoff, M. Ehrhardt, and K. Kremling, eds., Verlag Chemie, Weinheim, 1999, pp. 41–74.

[14] H.P. Hansen, *Determination of oxygen*, in *Methods of Sea Water Analyses*, K. Grasshoff, M. Ehrhardt, K. Kremling, eds., Verlag Chemie, Weinheim, 1999, pp. 75–90.

[15] L.G. Anderson, D.R. Turner, M. Wedborg, and D. Dyrssen, *Determination of alkalinity*, in *Methods of Sea Water Analyses*, K. Grasshoff, M. Ehrhardt, and K. Kremling, eds., Verlag Chemie, Weinheim, 1999, pp. 127–147.

[16] W.C. Krumbein and F.J. Pettijohn, eds, *Sedimentary petrography*, Appleton Century Crofts, Inc., New York, 1938, p. 349.

[17] H.E. Gaudette and W.R. Flight, *An inexpensive titration method of organic carbon in recent sediments*, J. Sed. Petrol. 44 (1974), pp. 249–253.

[18] D.W. Nelson and L.E. Sommers, *Total carbon, organic carbon, and organic matter*, in *Methods of Soil Analysis. Part 3: Chemical Methods,* D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert, P.N. Soltanpour, M.A. Tabatabai, C.T. Johnston, and M.E. Sumner, eds, American Society of Agronomy, Inc. and Soil Science Society of America, Inc., Madison, Wisconsin, 1996, pp. 961–1010.

[19] O.H. Lowry, N.J. Rosebrough, A.L. Fart, and R.J. Randall, *Protein measurement with Folin phenol reagent*, J. Biol. Chem. 193 (1951), pp. 265–275.

[20] D.L. Rice, *The detritus nitrogen problem: New observations and perspectives from organic geochemistry*, Mar. Ecol. Prog. Ser. 9 (1982), pp. 153–162.

[21] L.M. Mayer, L.L. Schick, and W. Frank Setchell, *Measurement of protein in nearshore marine sediments*, Mar. Ecol. Prog. Ser. 30 (1986), pp. 159–165.

[22] M. Dubois, K. Gilles, J.K. Hamilton, P.A. Rebers, and F. Smith, *Colorimetric method for determination of sugars and related substances*, Anal. Chem. 28 (1956), pp. 350–356.

[23] E.G. Bligh and W.J. Dyer, *A rapid method for total lipid extraction and purification*, Can. J. Biochem. Physiol. 37 (1959), pp. 911–917.

[24] H. Barnes and J. Blackstock, *Estimation of lipids in marine animals tissues: Detailed investigation of the sulphophosphovanillin method for "total" lipids*, J. Exp. Mar. Biol. Ecol. 12 (1973), pp. 103–118.

[25] R. Danovaro, M. Fabiano, and N. Della Croce, *Labile organic matter and microbial biomasses in deep-sea sediments (Eastern Mediterranean Sea)*, Deep-Sea Res. 40 (1993), pp. 953–965.

[26] S. Cividanes, M. Incera, and J. Lo'pez, *Temporal variability in the biochemical composition of sedimentary organic matter in an intertidal flat of the Galician coast (NW Spain)*, Oceanolog. Acta 25 (2002), pp. 1–12.

[27] M. Fabiano and R. Danovaro, *Composition of organic matter in sediments facing a river estuary (Tyrrhenian Sea): relationships with bacteria and microphytobenthic biomass*, Hydrobiologia 277 (1994), pp. 71–84.

[28] R. Fichez, *Composition and fate of organic matter in submarine cave sediments: Implications for the biogeochemical cycle of organic carbon*, Oceanolog. Acta 14 (1991), pp. 369–377.

[29] R.T. Nguyen and H.R. Harvey, *Preservation of protein in marine systems: Hydrophobic and other noncovalent associations as major stabilizing forces*, Geochim. Cosmochim. Acta 65 (2001), pp. 1467–1480.

[30] H. Knicker and P.G. Hatcher, *Sequestration of organic nitrogen in the sapropel from Mangrove lake, Bermuda*, Organic Geochem. 32 (2001), pp. 733–744.

[31] X. Zang, R.T. Nguyen, H.R. Harvey, H. Knicker, and P.G. Hatcher, *Preservation of proteinaceous material during the degradation of the green alga* Botryococcus braunii*: A solid-state 2D*^{15}N*,*^{13}C *NMR spectroscopy study*, Geochim. Cosmochim. Acta 65 (2001), pp. 3299–3305.

[32] F.G. Prahl, J.R. Ertel, M.A. Goni, M.A. Sparrow, and B. Eversmeyer, *Terrestrial organic carbon contributions to sediment on the Washington margin*, Geochim. Cosmochim. Acta 58 (1994), pp. 3035–3048.

[33] T.C. Jennerjahn and V. Ittekkot, *Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil: 1. Amino acids and hexosamine*, Oceanol. Acta 20 (1997), pp. 359–369.

[34] M. Yamamuro, *Chemical tracers of sediment organic matter origins in two coastal lagoons*, J. Mar. Syst. 26 (2000), pp. 127–134.
[35] P.J. Muller, *C/N ratios in Pacific deep sea sediments: Effect of inorganic ammonium and organic nitrogen compound sorbed by clays*, Geochim. Cosmochim. Acta 41 (1997), pp. 765–776.
[36] C. Barranguet, M.R. Plante-Cuny, and E. Alivon, *Microphytobenthos production in the Gulf of Fos, French Mediterranean coast*, Hydrobiologia 333 (1996), pp. 181–193.
[37] C.H. Lucas, J. Widdows, M.D. Brinsley, P.N. Salkeld, and P.M.J. Herman, *Benthic-pelagic exchange of microalgae at a tidal flat. 1. Pigment analysis*, Mar. Ecol. Prog. Ser. 196 (2000), pp. 59–73.
[38] W.D. Russel-Hunter, *Aquatic productivity: An introduction to some basic aspects of biological oceanography and limnology*, 306 pp., Collier-Macmillan, London, 1970.
[39] A. Verma and V. Subramanian, *Organic matter and amino acid concentrations in surface sediments of Vembanad Lake – a tropical estuary, west coast of India*, Reg. Environ. Change 2 (2002), pp. 143–149.
[40] R.C. Newell and J.G. Field, *The contribution of bacteria and detritus to carbon and nitrogen flow in a benthic community*, Mar. Biol. Lett. 4 (1983), pp. 23–36.
[41] A. Pusccedu, Origin, biochemical composition and fate of organic matter in marine environments with different trophic state. *PhD Dissertation*, University of Genova, Italy, 1997, 173 pp.
[42] Pusceddu, A. Dell'Anno, R. Danovaro, E. Manini, G. Sarà, and M. Fabiano, *Enzymatically hydrolyzable protein and carbohydrate sedimentary pools as indicators of the trophic state of detritus sink systems: A case study in the Mediterranean coastal lagoon*, Estuaries 26 (2003), pp. 641–650.
[43] Grémare, J.M. Amouroux, F. Charles, A. Dinet, C, Riaux-Gobin, J. Baudart, L. Medernach, J.Y. Bodiou, G. Vétion, and J.C. Colomines, *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 (1997), pp. 195–206.
[44] M. Fabiano and A. Pusceddu, *Total hydrolizable particulate organic matter (carbohydrates, proteins, and lipids) at a coastal station in Terra Nova Bay (Ross Sea, Antarctica)*, Polar Biol. 19 (1998), pp. 125–132.
[45] J.E. Cartes, A. Grémare, F. Maynou, S. Villora-Moreno, and A. Dinet, *Bathymetric changes in the distributions of particulate organic matter and associated fauna along a deep-sea transect down the Catalan sea slope (Northwestern Mediterranean)*, Prog. Oceanogr. 53 (2002), pp. 29–56.
[46] H.R. Harvey, J.H. Tuttle, and J.T. Bell, *Kinetics of phytoplankton decay during simulated sedimentation: Changes in biochemical composition and microbial activity under oxic and anoxic conditions*, Geochim. Cosmochim. Acta 59 (1995), pp. 3367–3378.