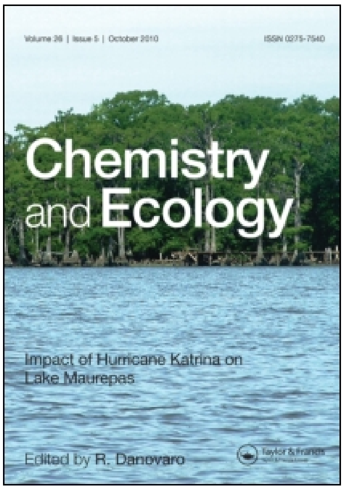

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Biogeochemical characteristics of the surface sediments along the western continental shelf of India

Josia Jacob[a]; K. A. Jayaraj[a]; H. Habeeb Rehman[a]; N. Chandramohanakumar[b]; K. K. Balachandran[a]; T. V. Raveendran[a]; Thresiamma Joseph[a]; Maheswari Nair[a]; C. T. Achuthankutty[a]
[a] National Institute of Oceanography, Regional Centre, Kochi, India [b] Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi, India

To cite this Article Jacob, Josia , Jayaraj, K. A. , Rehman, H. Habeeb , Chandramohanakumar, N. , Balachandran, K. K. , Raveendran, T. V. , Joseph, Thresiamma , Nair, Maheswari and Achuthankutty, C. T.(2009) 'Biogeochemical characteristics of the surface sediments along the western continental shelf of India', Chemistry and Ecology, 25: 2, 135 — 149

To link to this Article: DOI: 10.1080/02757540902758750

URL: http://dx.doi.org/10.1080/02757540902758750

Chemistry and Ecology
Vol. 25, No. 2, April 2009, 135–149

Biogeochemical characteristics of the surface sediments along the western continental shelf of India

Josia Jacob[a]*, K.A. Jayaraj[a], H. Habeeb Rehman[a], N. Chandramohanakumar[b], K.K. Balachandran[a], T.V. Raveendran[a], Thresiamma Joseph[a], Maheswari Nair[a] and C.T. Achuthankutty[a]

[a]*National Institute of Oceanography, Regional Centre, Dr. Salim Ali Road, Kochi, India;* [b]*Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, P.B. No. 1836, Fine Arts Avenue, Kochi, India*

(*Received 27 August 2008; final version received 19 January 2009*)

Surface sediments from the western continental shelf of India were analysed for total organic carbon (TOC), total nitrogen (TN), total hydrolysable carbohydrates (TCHO) and proteins (PRT) during the late summer monsoon (September–October, 2003) and pre-monsoon (March–April, 2004) seasons. The region experienced entirely different hydrographic characteristics and productivity patterns during the two seasons. Low oxygenated, cold, nutrient rich (DO $<180\,\mu$M, SST $<28°$C, $NO_3 > 2\,\mu$M) surface waters and the existence of subsurface suboxia were the hydrographic features during late summer due to the persistence of upwelling. Meanwhile, during pre-monsoon the region was oligotrophic and oxygen saturated (DO $>200\,\mu$M, $NO_3 < 2\,\mu$M). Satellite imagery, *in situ* Chl *a* and zooplankton biomass showed high production along the region during late summer compared to pre-monsoon. Sedimentary organic matter (SOM) was of marine origin during both seasons, as indicated by the C/N ratios. TCHO + PRT: TOC and PRT: TCHO revealed aged organic matter and did not change between the seasons. During late summer, TOC and the reactive organic matter (TCHO and PRT) in the surface sediments were concentrated along the regions (13–17° N) where active upwelling was observed, suggesting a close coupling between SOM characteristics and the surface ocean productivity.

Keywords: surface sediments; sedimentary organic matter; C/N ratios; late summer and pre-monsoon; continental shelf; India

1. Introduction

Continental margins, including the coastal area, shelf and slope, represent an important link between continents and the open sea, and play a vital role in the biogeochemical carbon cycle. More than 90% of all organic carbon burial presently occurs in continental margin sediments, making the margins one of the largest sinks in the global carbon budget [1,2]. The high organic matter content of the sediments adjacent to the continents relative to the open ocean results from a combination of higher primary production rates over continental margins, contributions from

*Corresponding author. Email: josiajacob@gmail.com

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540902758750
http://www.informaworld.com

terrigeneous sources, and the efficient export of that production to the shelf and slope regions [3,4]. Elemental composition and C/N ratios are frequently used as proxies for the sources of organic carbon in sediments [5,6]. Specific labile components of organic matter have been used to estimate the nutritional value of the sediment [7–9] and have profound implications on the organic matter diagenesis and turnover [10]. The role of the composition of organic matter in various coastal margin settings is a critical but poorly understood component of organic matter preservation in the oceans [11].

The western continental shelf of India experiences coastal upwelling during the summer monsoon period (June–September) [12,13]. The intensity and residence time of this coastal upwelling vary from south to north along the shelf as the summer monsoon progresses [14]. Upwelling is more intense between the southern tip of India (8° N) and Ratnagiri (17° N). When the upwelling intensifies along the western margin, oxygen is quickly depleted to near-zero levels in response to heterotrophic processes fuelled by high primary production, mainly within the pycnocline. Thus, the sub-pycnocline oxygen depletion is primarily of natural origin because the nutrient enrichment occurs mainly through upwelling, which sets in June, intensifies in September–October, and dissipates by December. This shallow and seasonal suboxic zone is distinct from the deeper, perennial suboxic layer of the central Arabian Sea. Oxygen deficiency in the region associated with the seasonal upwelling has intensified in recent years, due to enhanced nutrient loading by anthropogenic activities [15]. With the identification of the seasonal and shallow suboxic zone, the benthic-pelagic coupling and the organic matter accumulation in the surficial sediments of the western continental shelf has become important in explaining the biogeochemistry of the region [16].

The main objective of the present study is to compare the organic matter characteristics (total organic carbon content and the biochemical components – total hydrolysable carbohydrates and proteins) of the surface sediments during late summer (September–October) when the surface ocean production is high and the seasonal suboxia is prevalent along the region, and during pre-monsoon (April–May), when the shelf waters are oligotrophic and saturated with oxygen. The present study provides novel geochemical data of the surface sediments of the shelf which will help in a comprehensive understanding of the biogeochemistry of the region.

2. Study area

The continental shelf of the western India is a divergent and passive margin [17]. The shelf occupies an area of about 0.3×10^6 km^2 and extends from Kutch in the north (22.5° N) to Cape Comorin in the south (8° N) [18]. It is widest in the northern part, with a shelf width of about 300 km off Mumbai (19° N), which narrows to about 100 km off Ratnagiri (17° N). Progressive narrowing of the shelf is reflected in the 60 km wide shelf off Marmagoa (15° N) and 80 km wide shelf off Mangalore (13° N). The 80 km wide shelf off Kochi (10° N) again widens to 120 km at the southern tip of India, off Cape Comorin. Relatively perennial rivers like the Indus, the Narmada and the Tapti supply large amounts of sediments to this shelf [19]. Many small rivers, like the Mandovi and Zuari in Goa, the Kalinadi in north Kanara, and the Netravati in south Kanara, flow across the coastal plain, most of which are estuarine for the greater part of their length [20].

3. Methodology

3.1. *Sampling*

Surface sediment samples were collected from 15 locations during late summer, 2003 (September–October), and pre-monsoon, 2004 (April–May) along the western continental shelf of India onboard FORV Sagar Sampada (Figure 1). Sampling was done from seven latitudes – one sample from the inner shelf (∼50 m water depth) and the other representing the outer shelf (∼150 m water depth) from each latitude, except from the outershelf of 8° N during late summer and the outershelf of 22° N during pre-monsoon season, respectively. Sediments were collected using a Smith McIntyre grab supplemented with external lead weights, having an area of 0.1 m^2. The vessel was stopped during the sampling, and the sampling was repeated until the grab was completely filled to retrieve intact surface sediment layers. The surface sediment layers (0–1 cm) were immediately stored at −20° C. Before analysis, samples were thawed, air-dried and ground to a fine powder. Water samples above the grab stations were collected from standard depths (0, 10, 20, 30, 50, 75, 100, 150 m), using a 1.7L Niskin sampler fitted to a Sea Bird Conductivity–Temperature–Depth (CTD) rosette system. Zooplankton samples were collected with a Multiple Plankton Closing Net (Hydro-Bios; mouth area 0.25 m^2 and mesh width 200 μm).

3.2. *Laboratory analysis*

The total organic carbon (TOC) content was determined after acidification of the dry sediment samples [21]. HCl (1M) was added until cessation of effervescence upon acid addition, which indicated a complete removal of inorganic carbon. TOC and total nitrogen (TN) were subsequently measured using a CHN elemental analyser (VarioEL III). Total hydrolysable carbohydrates (TCHO) were analysed according to [22], after hydrolysis of the sediment samples with 1N H_2SO_4 for 1 h,

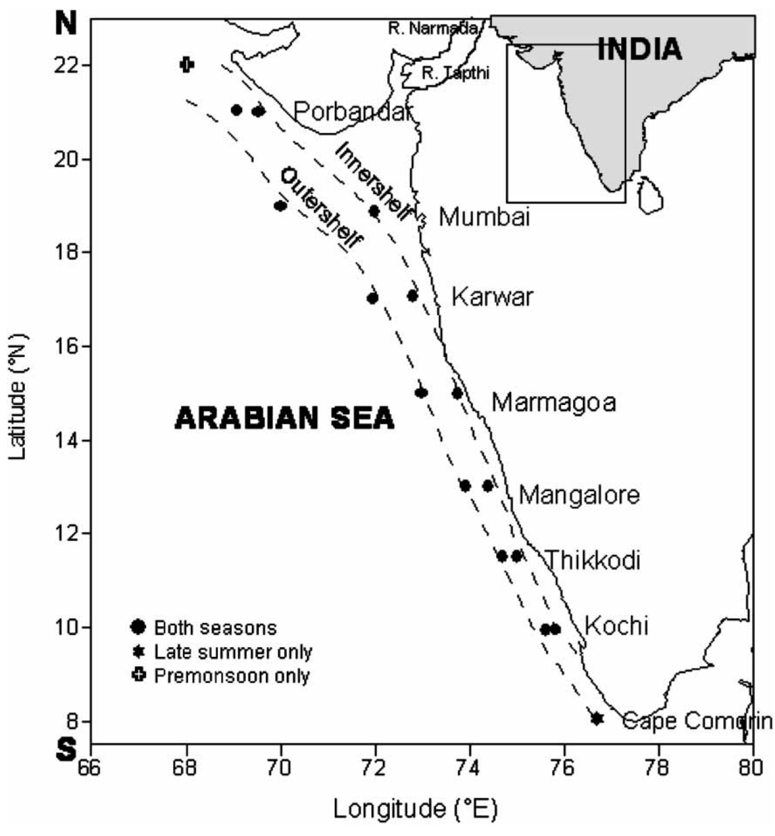

Figure 1. Map showing the station locations.

and expressed as glucose equivalents. The standard deviation for triplicate analyses was found to be 4.5%. Proteins (PRT) were analysed according to [23] as modified by [24] to account for the reactivity of phenolic compounds, after extraction with 1N NaOH for 30 min, and the protein concentrations were given as bovine serum albumin equivalents. Triplicate analyses of the samples gave a standard deviation of 5.3%. Sediment samples previously heated in a muffle furnace at 450°C for 6 h were used as the blanks for all the biochemical analyses and were analysed the same as the samples. TCHO and PRT were converted into carbon equivalents using conversion factors of 0.40 and 0.49 [7,25]. The textural characteristics (sand, silt and clay) were determined by pipette analysis [26] after removing the inorganic carbonates using 10% HCl and organic matter using 15% H_2O_2. The results are expressed as the average of triplicate analysis. The analysis for the dissolved oxygen in the water samples was done by the Winkler method and the dissolved inorganic nutrients (nitrate and nitrite) were measured using a SKALAR 4-channel autoanalyser onboard, following standard procedures [27]. Chlorophyll *a* (Chl *a*) was analysed [28] using a spectrophotometer (Schimadzu UV/VIS 1650PC). Zooplankton biomass was calculated using the displacement volume method. For this, the zooplankton sample was filtered through a clean, dried netting material (200 μm). The interstitial water was removed with blotting paper. The filtered zooplankton was then transferred to a measuring cylinder with a known volume of 4% formalin – seawater solution. The displacement volume was obtained by recording the volume of fixative in the measuring jar displaced by the zooplankton from which biomass was calculated [29]. In addition, chlorophyll monthly average imageries for September 2003, October 2003 and April 2004 were obtained from SeaWiFS.

Pearson correlation analysis was carried out to test the relationships among the various sedimentary parameters during the two sampling periods using SPSS release 7.5. Spatial (depth vs. latitude) and temporal (seasons vs. latitude) changes in the organic matter, its labile constituents and the texture of the sediments were tested by two-way ANOVA. Temporal variations were also tested for Chl *a* and zooplankton biomass.

4. Results

4.1. *Hydrochemical characteristics of the shelf region*

The distribution of sea surface temperature (SST), dissolved oxygen (DO), nitrite (NO_2) and nitrate (NO_3) along the western continental shelf during late summer monsoon shows that the shelf waters between 11–18° N were characterised by cool (SST <26°C), low oxygenated (DO <190 μM) and nutrient rich waters ([NO^{3-}] >2 μM) (Figure (2)). The 190 μM of DO found at ∼15 m depth along 8° N, surfaced along 15° N but then deepened to 35 m beyond 19° N (Figure 2(a)ii). Similar trends were observed for 26°C isotherm and the 2 μM nitrate, suggesting that upwelling was still prominent even during the late phase of summer monsoon (Figure 2(a)i and iii). The entire shelf was characterised by oxygen deficient subsurface waters, but much lower values (DO <10 μM) were observed at the intermediate depths along the inner shelf (20–30 m between 13 and 16° N) and the outer shelf (100–150 m at 14–19° N) (Figure 2(a)ii and 2(b)ii). Intense denitrification was also observed in the subsurface waters of the inner shelf, as evidenced by a large nitrite concentration which comprised between 1 and 4 μM (Figure 2(a)iv).

During pre-monsoon, the shelf waters were saturated with oxygen (DO >200 μM) and devoid of nutrients ([NO^{3-}] <2 μM) (Figure 3). The intermediate waters (beyond 170 m) of the outer shelf had low oxygen content (<20 μM) (Figure 3(b)ii). Slight upsloping of the isolines of SST, DO and nitrate was found towards the northern latitudes (Figure 3(b)).

During the late summer, DO in the bottom waters were low along both the outer shelf (13.94(av) ± 5.39 (sd) μM) and the inner shelf (27.80 ± 25.67μM). Intense oxygen deficiency

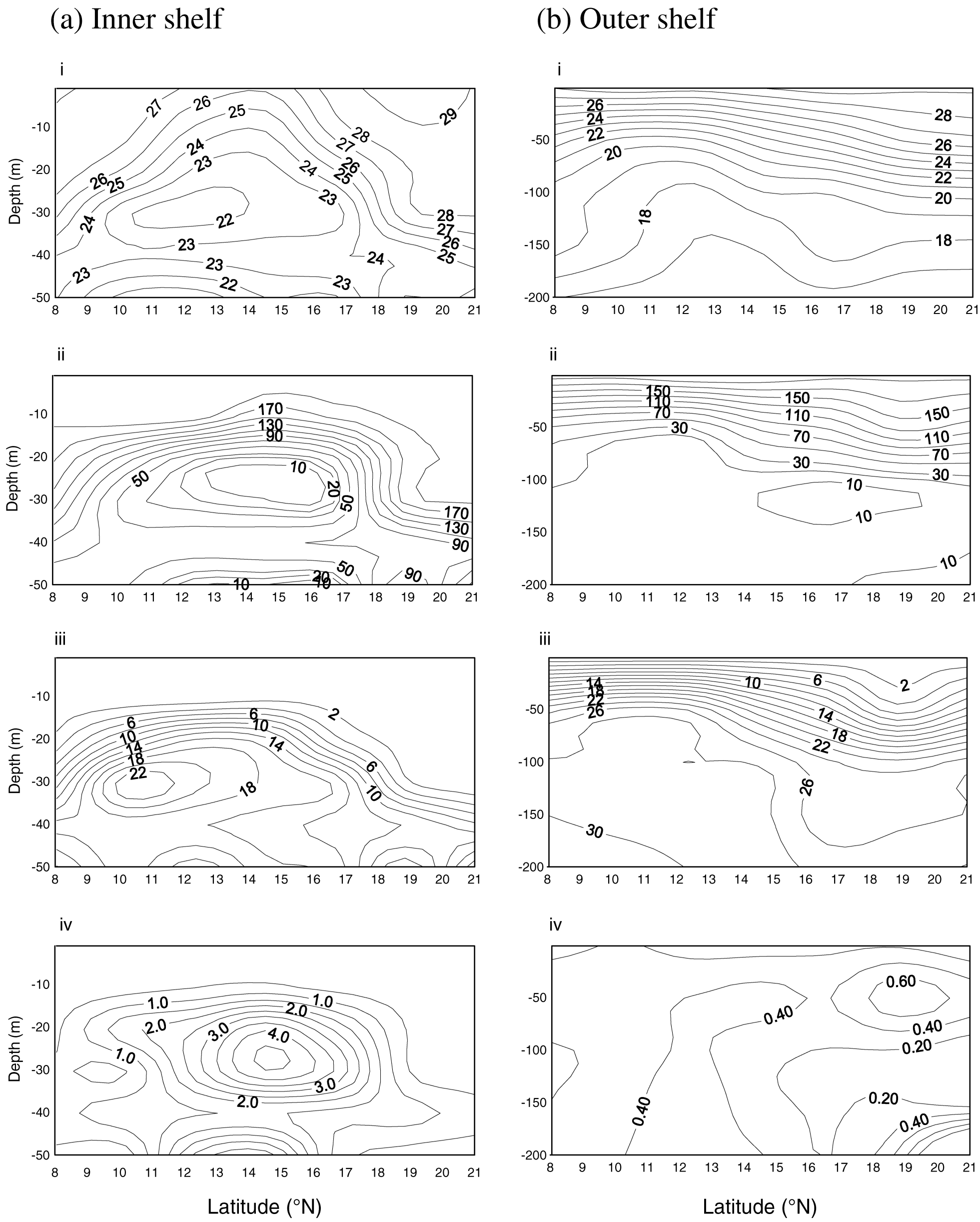

Figure 2. Distribution of: i. temperature (°C), ii. dissolved oxygen (μM), iii. nitrate (μM), and iv. nitrite (μM) (a) along the inner shelf and (b) the outer shelf during late summer monsoon.

was observed along 11.5–17° N (DO <15 μM) (Figure 4(a)). Salinity of the bottom waters were in the range 34.93–36.34 (35.43 ± 0.52) (Figure 4(b)). The bottom water temperature was found to be similar along both the outer shelf (18.15 ± 2.55°C) and the inner shelf (21.34 ± 2.53°C) during late summer monsoon (Figure 4(c)).

During pre-monsoon, DO contents of the bottom waters along the outer shelf (44.20 ± 51.13 μM) and the inner shelf (162.87 ± 26.56 μM) were comparatively higher. The lowest DO was observed in the bottom waters of 13, 15, 17 and 19° N (DO <10 μM) (Figure 4(d)). The

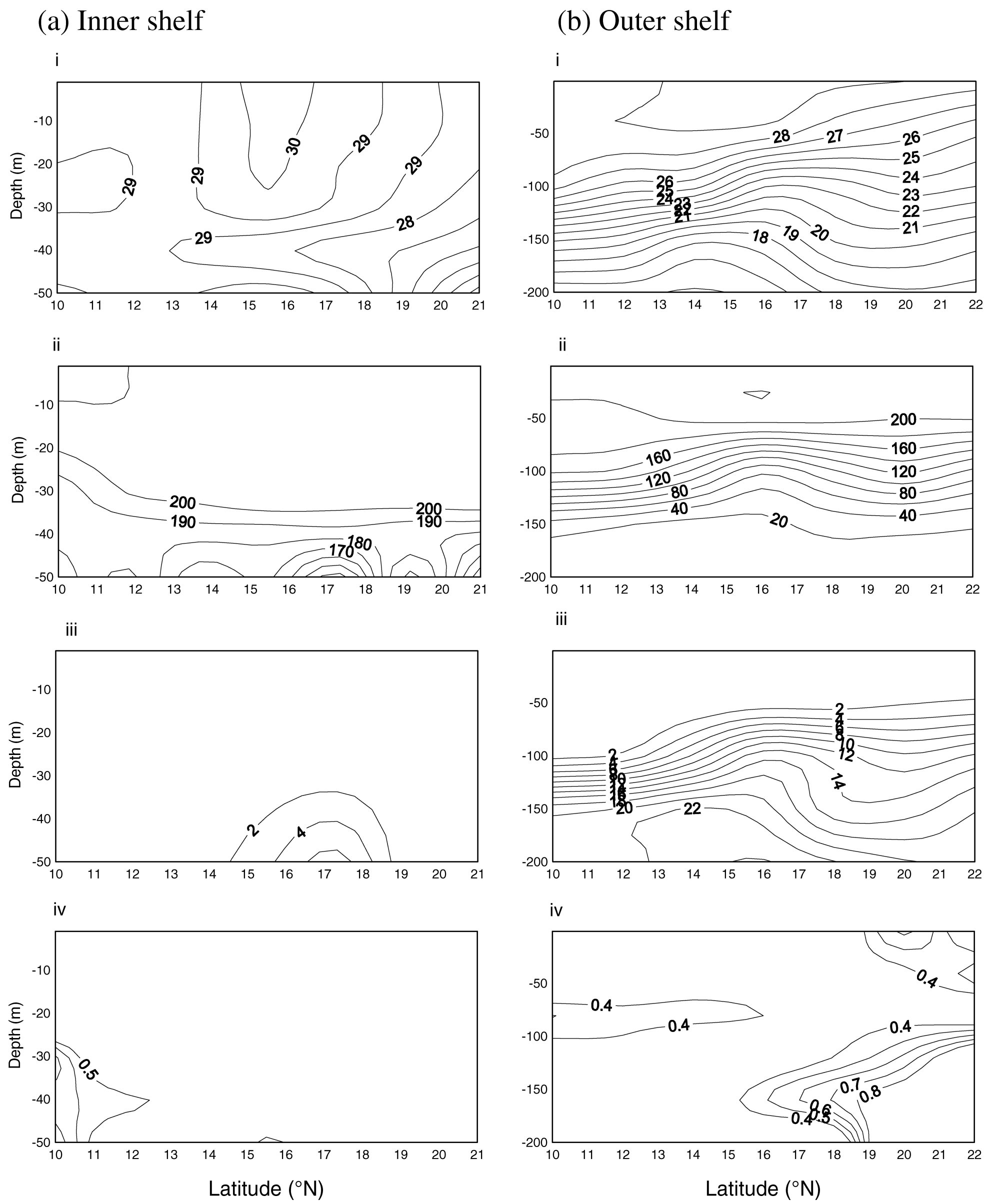

Figure 3. Distribution of: i. temperature (°C), ii. dissolved oxygen (μM), iii. nitrate (μM), and iv. nitrite (μM) (a) along the inner shelf and (b) the outer shelf during pre-monsoon.

salinity of the bottom waters ranged from 34.40 to 36.46 (35.55 ± 0.49) (Figure 4(e)). The temperature also increased along the outer shelf (14.5–27.7°C) and the inner shelf (25.25–29.48°C) (Figure 4(f)).

4.2. *Biological production*

SeaWiFS imagery showed high biomass of Chl *a* along 12–18° N in the west coast of India during September 2003 (Figure 5(a)). In October 2003, however, the satellite imagery showed a

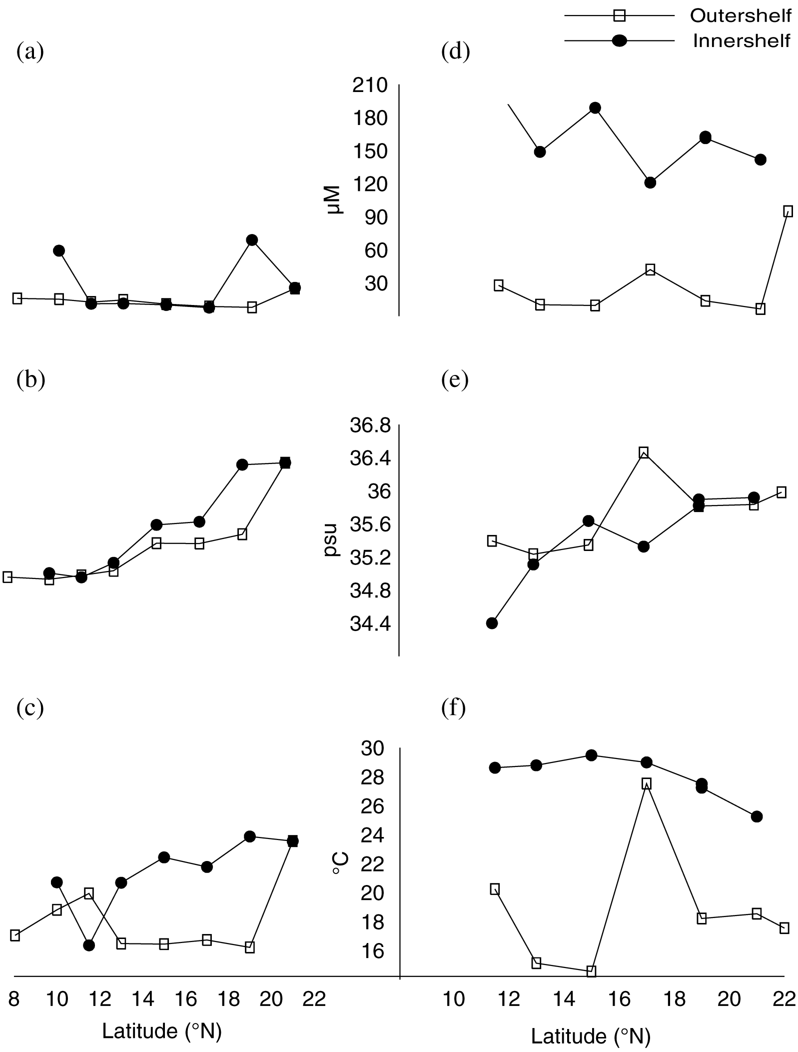

Figure 4. Distribution of (a) dissolved oxygen (µM), (b) salinity, (c) temperature (°C) in the bottom waters during late summer and distribution of (d) dissolved oxygen (µM), (e) salinity, (f) temperature (°C) in the bottom waters of the shelf during pre-monsoon.

latitudinal shift in the high production region towards the north (13–19° N) (Figure 5(b)). During April 2004, lower concentrations of Chl *a* were observed along the entire shelf than during the late summer monsoon. But the northernmost transects showed slightly higher Chl *a* values than the south (Figure 5(c)).

In situ surface Chl *a* along the outer shelf regions during late summer were in the range 0.12–0.75 mg/m^3 (0.42 ± 0.25) (Figure 6(a)) with high values along 10, 13 and 17° N. 15° N showed low Chl *a* when compared to the adjacent stations. Chl *a* along the outer shelf during pre-monsoon were low ($0.24 \pm 0.16\,mg/m^3$) on average, compared to late summer (Figure 6(e)).

The distribution of zooplankton biomass in the mixed layer depth along the outer shelf during late summer was also considerably higher ($0.56 \pm 0.34\,ml/m^3$) when compared with pre-monsoon ($0.16 \pm 0.08\,ml/m^3$) (Figures 6(b) and (f)). The distribution of ostracods during

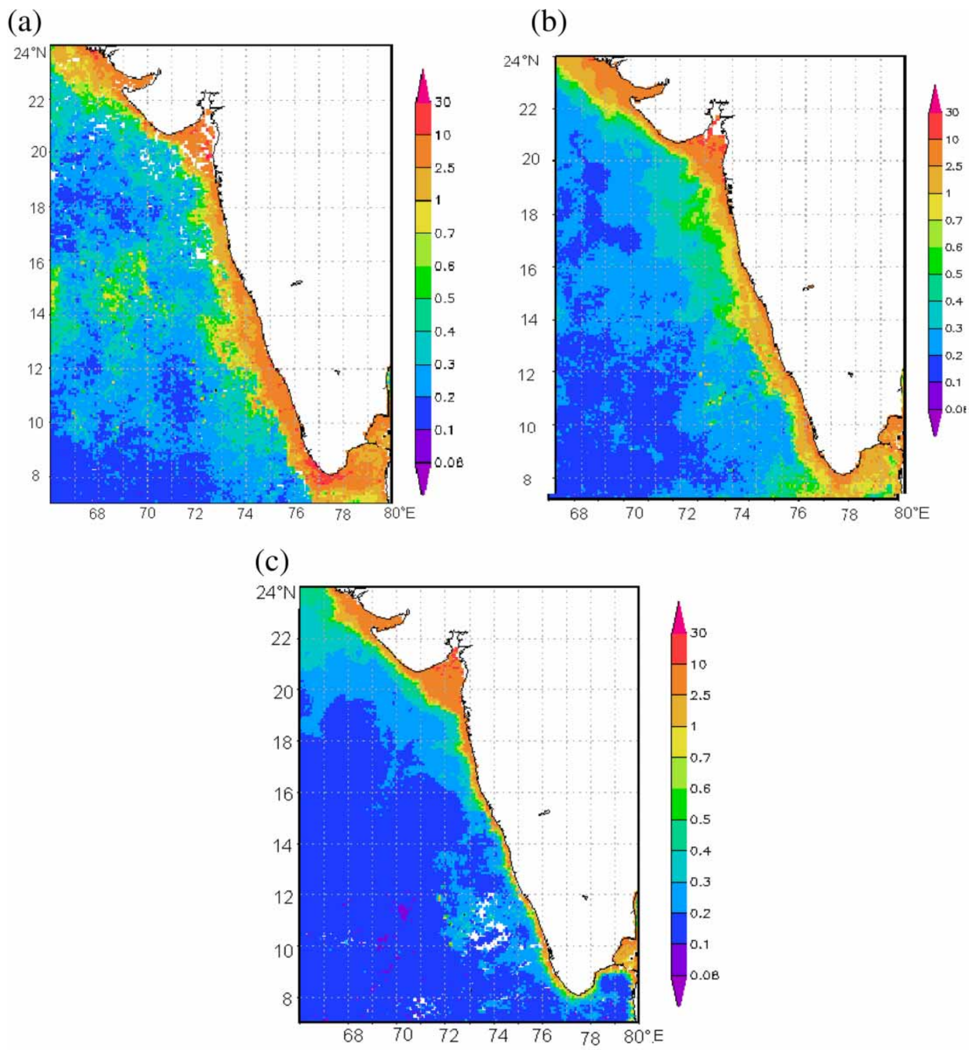

Figure 5. Satellite imagery (SeaWiFS monthly average) of Chl *a* (mg/m^3) during (a) September 2003, (b) October 2003, and (c) April 2004.

late summer shows abundance from 8–15° N, whereas copelates were found along 11.5–21° N except at 19° N (Figures 6(c) and (d)).

4.3. *Textural characteristics*

The average sand, silt and clay percentages were 39.19 ± 30.00, 44.56 ± 28.00 and 16.04 ± 12.21, respectively, during the late summer monsoon season. Fine particles (silt + clay) dominated north of 11.5° N during the late summer, where the average percentage was found to be 77.56 ± 20.18 and the average sand percentage was 19.30 ± 12.90 (Table 1). A dominance of sand (48.90 ± 34.22%) and silt (39.80 ± 35.54%) were observed during the pre-monsoon season (Table 2).

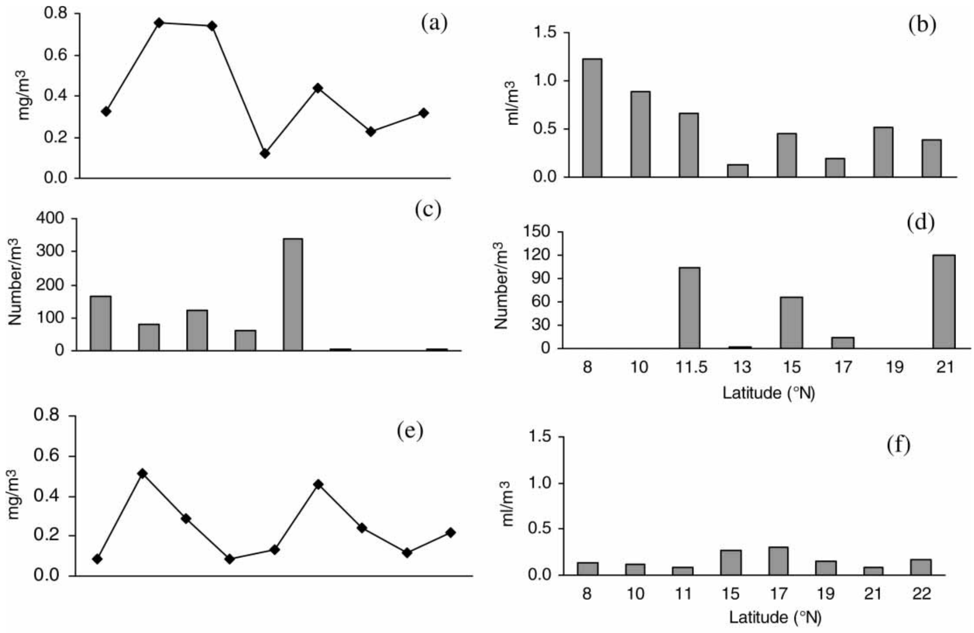

Figure 6. Distribution of (a) surface Chl *a* (mg/m^3), (b) zooplankton biomass (ml/m^3), (c) ostracoda (Number/m^3) and (d) copelata (Number/m^3) during late summer, and distribution of (e) surface Chl *a* (mg/m^3) and (f) zooplankton biomass (ml/m^3) during pre-monsoon along the outer shelf.

4.4. *Total organic carbon*

During late summer, the average total organic carbon (TOC) content in the surficial sediments was 12.78 ± 9.77 mg/g. TOC was maximum along the outer shelf of 15° N (36.70 mg/g) and 17° N (28.38 mg/g) (Figure 7(a)). During pre-monsoon, the average TOC was 10.84 ± 4.63 with an exceptionally high value at the outer shelf of 15° N (35.34 mg/g) (Figure 7(d)).

Table 1. Distribution of the texture, PRT/TCHO, [(PRT−C + TCHO−C): TOC]%, TN and C/N of the surface sediments from the western continental shelf of India during late summer.

	Stn. No	Latitude (°′N)	Longitude (°′E)	Sand (%)	Silt (%)	Clay (%)	PRT/ TCHO	[(PRT−C + TCHO −C): TOC]%	TN (%)	C/N
Outershelf	1	8 03.11	76 41.66	69.13	12.82	18.05	0.15	8.24	0.15	7.62
	2	9 55.90	75 36.42	80.07	14.43	2.50	0.07	10.32	0.10	8.28
	3	11 29.82	74 42.13	54.36	28.14	17.50	0.12	9.61	0.16	8.46
	4	12 59.93	73 55.38	50.86	15.28	33.86	0.17	8.84	0.14	7.89
	5	15 00.00	72 59.05	16.57	53.65	29.78	0.17	7.89	0.33	13.35
	6	16 59.81	71 57.58	17.63	41.87	40.50	0.16	6.12	0.37	9.21
	7	18 59.82	70 0.45	19.81	67.69	12.50	0.08	12.63	0.05	9.65
	8	21 01.86	69 4.43	60.32	34.68	5.00	0.16	12.19	0.07	7.96
Innershelf	9	9 56.52	75 48.94	83.61	<0.2	16.14	0.11	13.13	0.11	4.64
	10	11 30.09	75 0.05	76.36	14.26	9.38	0.14	9.63	0.11	5.65
	11	13 0.36	74 24.17	28.19	51.81	20.00	0.15	11.79	0.21	7.17
	12	14 58.85	73 44.87	<0.2	72.3	27.50	0.08	16.41	0.37	8.36
	13	17 03.45	72 48.57	26.16	63.95	9.89	0.12	7.93	0.25	6.66
	14	18 51.96	71 59.81	4.12	85.88	10.00	0.18	7.43	0.13	7.85
	15	20 59.42	69 32.76	<0.5	95.5	4.00	0.15	13.38	0.21	6.35

Table 2. Distribution of the texture, PRT/TCHO, [(PRT−C + TCHO−C): TOC]%, TN and C/N of the surface sediments from the western continental shelf of India during pre-monsoon.

	Stn. No	Latitude (°′N)	Longitude (°′E)	Sand (%)	Silt (%)	Clay (%)	PRT/ TCHO	[(PRT−C + TCHO −C): TOC]%	TN (%)	C/N
Outershelf	16	9 59.48	75 38.30	70.77	9.35	19.87	0.13	7.87	0.17	6.14
	17	11 28.90	74 43.31	53.45	33.00	13.55	0.06	10.47	0.19	7.12
	18	12 59.33	73 54.45	29.44	49.50	21.06	0.19	6.29	0.21	8.96
	19	14 59.86	73 00.24	26.26	72.24	1.50	0.21	7.07	0.27	15.71
	20	16 59.80	72 04.34	95.93	0.87	3.20	0.08	9.42	0.09	7.56
	21	19 00.05	70 00.83	89.06	8.84	2.10	0.17	8.15	0.14	7.00
	22	20 59.31	69 10.16	1.65	94.58	3.77	0.08	11.85	0.22	7.64
	23	22 00.96	68 00.44	4.80	87.80	7.50	0.05	8.61	0.17	13.26
Innershelf	24	9 59.06	75 48.78	62.00	25.50	12.50	0.12	10.78	0.14	4.81
	25	11 30.57	75 09.94	75.60	7.90	16.50	0.12	8.26	0.15	6.36
	26	13 00.32	74 24.19	51.84	17.63	30.53	0.24	8.59	0.22	8.57
	27	14 58.00	73 42.00	51.90	42.80	5.30	0.18	8.98	0.20	7.25
	28	17 00.03	73 00.24	0.90	94.10	5.00	0.11	14.81	0.24	9.06
	29	18 46.67	71 46.26	69.22	9.28	21.50	0.27	13.97	0.13	6.07
	30	20 59.85	69 30.52	2.10	83.93	13.97	0.11	13.72	0.21	5.23

4.5. *Total carbohydrates*

Total hydrolysable carbohydrates (TCHO) were concentrated along 13–17° N during late summer, with an average of 2.74 ± 2.30 mg/g along the shelf. TCHO was maximum along the inner shelf (9.57 mg/g) and the outer shelf (5.99 mg/g) of 15° N during the season (Figure 7(b)). The average TCHO along the shelf during pre-monsoon was 2.51 ± 1.44 mg/g with maximum along the inner shelf at 17° N (5.88 mg/g) and the outer shelf at 15° N (4.99 mg/g) (Figure 7(e)).

4.6. *Protein*

The average protein content (PRT) of the shelf sediments was 0.35 ± 0.26 mg/g during the late summer monsoon and 0.34 ± 0.25 mg/g during the pre-monsoon season. PRT was maximum along the outer shelf (1.02 mg/g) and the inner shelf at 15° N (0.76 mg/g) during late summer, whereas it was maximum along the outer shelf at 15° N (1.03 mg/g) and inner shelf at 17° N (0.68 mg/g) during pre-monsoon (Figure 7(c) and (f)).

A spatial enrichment in TOC and its labile constituents (TCHO and PRT) were observed along 13–17° N during late summer. Whereas TOC and its labile constituents were higher along the outer shelf of 15° N and the inner shelf of 17° N during pre-monsoon, their distribution pattern did not follow any similar trend.

4.7. *Total nitrogen and C/N*

TN ranged from 0.05–0.37% (0.18 ± 0.10) during late summer and 0.09 to 0.27% (0.18 ± 0.05) during pre-monsoon. C/N ratios varied from 4.64–9.65 (7.94 ± 1.99) except at the outer shelf at 15° N (13.35) during late summer. During premonsoon, C/N ranged from 4.81–13.26 (8.05 ± 2.92), except in the outer shelf region at 15° N where the C/N ratio was 15.71 (Tables 1 and 2).

4.8. *Statistical analysis*

During both seasons, there was significant correlation ($p < 0.01$) between TOC and PRT and between TOC and TCHO. PRT and TCHO were also significantly correlated with each other

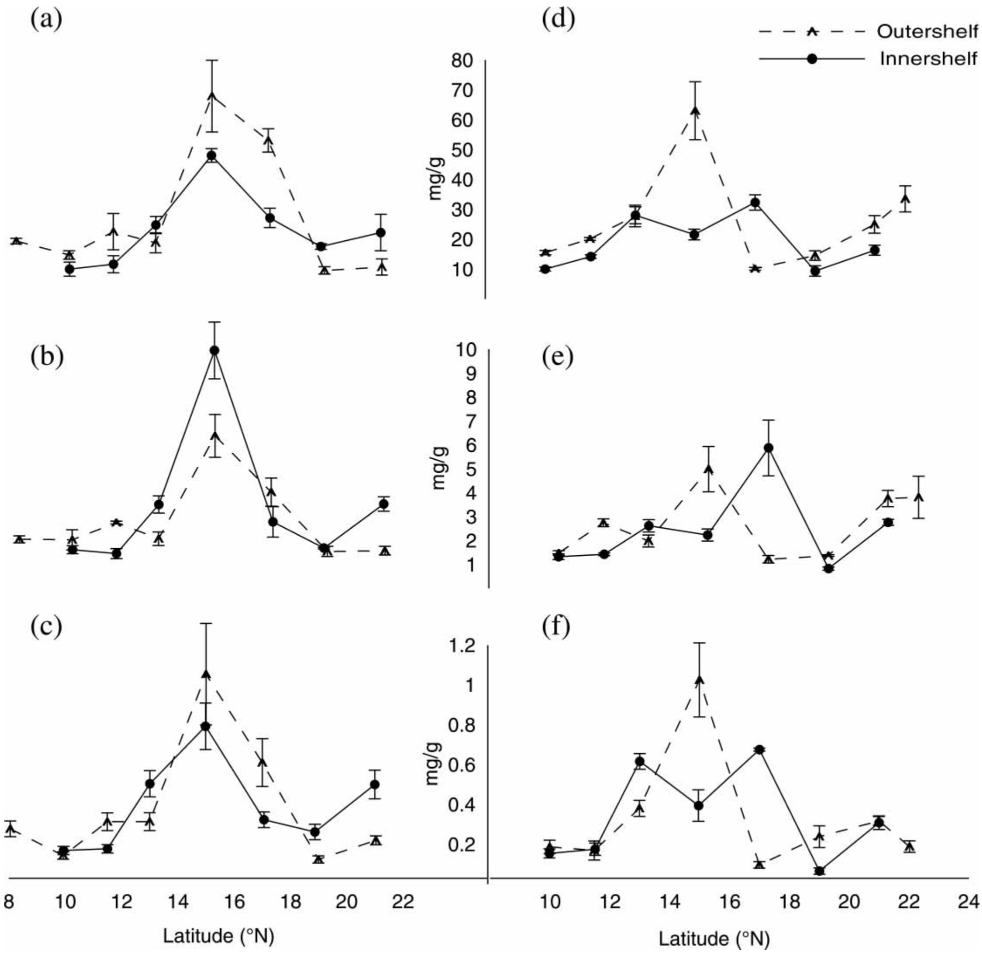

Figure 7. Distribution of (a) TOC, (b) TCHO, and (c) PRT during late summer monsoon, and distribution of (d) TOC, (e) TCHO, and (f) PRT during pre-monsoon.

Table 3. Pearson correlation among the measured parameters ($n = 15$).

		TOC	PRT	TCHO	Sand	Silt	Clay	TN
Late summer	TOC	1.00	0.95**	0.80**	−0.55	0.29	0.69**	0.95**
	PRT	0.95**	1.00	0.85**	−0.61	0.39	0.60*	0.89**
	TCHO	0.80**	0.85**	1.00	−0.57	0.39	0.49	0.85**
	Sand	−0.55*	−0.61*	−0.57*	1.00	−0.93	−0.26	−0.60*
	Silt	0.29	0.39	0.39	−0.93**	1.00	−0.11	0.35
	Clay	0.69**	0.60*	0.49	−0.26	−0.11	1.00	0.70**
	TN	0.95**	0.89**	0.85**	−0.60**	0.34	0.70**	1.00
Premonsoon	TOC	1.00	0.83**	0.80**	−0.59*	0.61*	−0.17	0.86**
	PRT	0.83**	1.00	0.71**	−0.46	0.43	0.04	0.77**
	TCHO	0.80**	0.71**	1.00	−0.82**	0.85**	−0.24	0.78**
	Sand	−0.59*	−0.46	−0.82**	1.00	−0.97**	0.02	−0.68**
	Silt	0.61*	0.43	0.85**	−0.97**	1.00	−0.27	0.66**
	Clay	0.17	0.04	−0.24	0.02	−0.27	1.00	0.01
	TN	0.86**	0.77**	0.78**	−0.68**	0.66**	−0.01	1.00

Note: Significance levels: *$0.05 > p > 0.01$; **$0.01 > p > 0.001$.

($p < 0.01$). TN was positively correlated with TOC and its labile constituents (TCHO and PRT) during both seasons ($p < 0.01$). TOC, TCHO and PRT were negatively correlated to sand content during both seasons, which implies the significance of fine-grained sediment texture in OC preservation. During late summer, TOC, TCHO and PRT were correlated with clay ($p < 0.01$), whereas during premonsoon season, TOC was correlated with silt ($p < 0.05$) (Table 3). Significant latitudinal variations were observed for TOC ($F = 5.65,\ p > 0.01$), TCHO ($F = 5.35,\ p > 0.01$) and PRT ($F = 6.30,\ p > 0.01$) during late summer. No significant temporal (seasonal) variation ($p > 0.05$) were observed for TOC and its labile constituents (TCHO and PRT), but significant temporal variations were observed for zooplankton biomass ($F = 7.35,\ p > 0.01$).

5. Discussion

During late summer monsoon season, the shelf waters of the west coast of India experienced intense upwelling along 11–18° N, as evidenced from the cool, low oxygenated and nutrient rich surface waters. Enhanced biological production with relatively colder, nutrient rich waters advecting to the mixed layers is typical of the region until October [30–32]. The SeaWiFS imagery shows high production over the entire continental shelf, especially along 12–19° N during late summer monsoon sampling compared to the pre-monsoon sampling. *In situ* surface Chl *a* distributions during the same late summer monsoon sampling show maximum production along 10–17° N, except at 15° N. Low surface production along 15° N, even when nutrient concentrations were high, was observed during the same season by Naqvi [16]. High zooplankton biomass in the mixed layer (MLD) was also observed along the shelf during late summer. However, low zooplankton biomass along 13–19° N may be due to the presence of suboxic waters, which restrict the zooplankton to the MLD (<10 m). The abundance of copelates along 11.5–21° N may also indicate high production, since they are filter feeders found in the euphotic zone [33]. Ostracods were found to occur along 8–15° N, which suggest contributions from detrital material [34] in the water column of these latitudes.

Elevated export fluxes and high sedimentation rates have been observed in the Arabian Sea, especially along the margins, during SW monsoon [35–38]. Hence, large amounts of organic matter are exported from the surface layers to sediments of these transects (13–17° N). This leads to intense remineralisation of organic matter in the subsurface layers of these transects, as evidenced from the intense oxygen deficiency (DO $<10\,\mu$M) and denitrification ($[NO^{2-}] > 5\,\mu$M), which extends to the bottom waters.

The surface sediments along these transects (13–17° N) had high concentrations of TOC when compared to other latitudes. The reactive (labile) organic matter, as reflected by the PRT and TCHO content, closely followed a trend similar to TOC. Spatial patterns in surface production closely followed SOM characteristics (bulk and reactive organic matter) during the highly productive late summer. The settling flux of organic carbon, which is closely tied to primary productivity, furnishes the principal control on the accumulation of OM in marine sediments [39–41]. The spatial variation in bulk and reactive organic matter are likely due to differences in the intensity of upwelling and associated primary production during late summer monsoon. This is supported by a close coupling between the bulk and reactive organic matter in the sediments with enhanced surface productivity, as observed along the shelf during late summer.

The C/N ratio (6:14) suggests that the sedimentary organic matter was mostly of marine origin [42]. The influence of SW monsoon driven productivity and resultant benthic-pelagic coupling is observed even in the pelagic sites of Arabian Sea, as illustrated by the close correlation of mean annual primary productivity in the surface waters with the distribution of chlorophyll *a* and organic matter composition (PRT content) of surface sediments [43]. However in the present study, the percentage of reactive organic matter (labile fraction) was similar during both late summer

(10.37 ± 2.81% of OM) and pre-monsoon seasons (9.92 ± 2.61% of OM). The ratio PRT:TCHO was low during both seasons (0.133 ± 0.035 during late summer and 0.14 ± 0.065 during pre-monsoon), which indicates aged and/or refractory OM [44]. The contribution of hydrolysable amino acids and carbohydrates to TOC in the surface sediments of Oman margin was also found to be low. Hence, it was hypothesised that the OM in the Oman margin sediments within the oxygen minimum zone (OMZ) was mostly of refractory composition, due to the long residence time of sinking particles in the water column [45–47]. In contrast, OM in sediments from the Peru Margin upwelling zone is mostly labile [48,49]. Further, the degradation rates for labile organic matter (such as PRT) have been found to be similar under oxic and anoxic conditions in several sedimentary settings [50–52]. It has also been shown that long-term degradation of OM is further reduced under permanently oxic or anoxic conditions than when it is exposed to alternating oxic/anoxic redox transitions [53,54]. The hypothesis based on our observation is that the remineralisation of organic matter is high along the southeast margin of the Arabian Sea even during the changing redox conditions and hence the OM in the surface sediments is mostly refractory.

The western continental shelf of India was oligotrophic and oxygen saturated during pre-monsoon. The region is sustained by the lowest primary productivity during the season [55]. But, frequent phytoplankton blooms, mainly *Trichodesmium* sp., are a characteristic of the region during the season [56]. Zooplankton biomass and *in situ* Chl *a* were less during the season compared to late summer. SeaWiFS imagery also showed lower production along the shelf during pre-monsoon but the northernmost transects showed slightly higher Chl *a* values. Slight upsloping of the isolines of SST, DO and nitrate was also found towards the northern latitudes, which may be the effect of the winter cooling which prevailed in the region. Even though the outer shelf of 15° N and the inner shelf of 17° N had high TOM, TCHO and PRT in the surface sediments, no coupling of SOM characteristics with surface productivity or water column characteristics were observed during the season. Besides surface production, sedimentation rates, transport processes, diagenesis, depositional environment, oxygen content, sediment mixing, etc. are thought to control the preservation and accumulation of OM in surface sediments [39–41,57,58]. Further research based on isotopic and biomarker studies will give a better insight to the seasonal and spatial variations in the organic matter characteristics and their sources into the region.

6. Conclusion

The western continental shelf of India was found to be a highly dynamic system with varying hydrographical conditions and productivity patterns during the seasons investigated. Enrichment of sedimentary organic matter and reactive OM (TCHO and PRT) in the surface sediments reflects the spatial changes in the surface ocean productivity during the late summer monsoon season. Hence, a strong response of the bulk and reactive organic matter to the surface ocean productivity was observed during late summer monsoon sampling. Despite high production and seasonal suboxia in the water column, the surface sediments had aged OM with low labile components, which may indicate intense OM remineralisation in the environment. The present study provides a better understanding of the organic matter accumulation and its labile composition in the surface sediments during the development of the seasonal suboxia and the highly productive upwelling season along the western continental shelf of India.

Acknowledgements

The authors would like to thank the Director, National Institute of Oceanography, Goa for providing the facilities for the study. We are grateful to all the participants of the cruise for their cooperation in sampling. This investigation was carried out under the programme ‘Environment and Productivity Patterns in the Indian EEZ’, funded by the Ministry of Ocean Development, CMLRE, Kochi, India. The first author is deeply indebted to the Council of Scientific and Industrial Research, New Delhi, India for the financial assistance. This is NIO contribution number 4507.

References

[1] J.I. Hedges and R.G. Keil, *Sedimentary organic matter preservation: An assessment and speculative synthesis*, Mar. Chem. 49 (1995), pp. 81–115.
[2] H. de Haas, T.C.E. van Weering, and H. de Stieger, *Organic carbon in shelf seas: Sinks or sources, processes and products*, Cont. Shelf Res. 22 (2002), pp. 691–717.
[3] R.W. Eppley and B.J. Peterson, *Particulate organic matter flux and planktonic new production in the deep ocean*, Nature 282 (1979), pp. 677–680.
[4] J.J. Walsh, *Importance of continental margins in the marine biogeochemical cycle of carbon and nitrogen*, Nature 350 (1991), pp. 53–55.
[5] J.J. Middelburg and J. Nieuwenhuize, *Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary*, Mar Chem. 60 (1998), pp. 217–225.
[6] E.S. Gordon and M.A. Goñi, *Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico*, Geochim. Cosmochim. Acta 67 (2003), pp. 2359–2375.
[7] M. Fabiano, R. Danovaro, and S. Fraschett, *A three-year time series of elemental and biochemical composition of organic matter in the subtidal sandy sediments of the Lingurian Sea (North Western Mediterranean)*, Cont. shelf Res. 15 (1995), pp. 1453–1469.
[8] S. Cividanes, M. Incera, and J. Lopez, *Temporal variability in the biochemical composition of sedimentary organic matter in an intertidal flat of the Galician coast (NW Spain)*, Oceanol. Acta 25 (2002), pp. 1–12.
[9] M. Incera, S.P. Cividanes, M. Lastra, and J. Lopez, *Temporal and spatial variability of sedimentary organic matter in sandy beaches on the northwest coast of the Iberian Peninsula*, Estuar. Coast. Shelf Sci. 58 (2003), pp. 55–61.
[10] G.T. Rowe and J.W. Deming, *The role of bacteria in the turnover of organic carbon in deep-sea sediments*, J. Mar. Res. 43 (1985), pp. 925–950.
[11] M.A. Goñi, M.B. Yunker, R.W. Macdonald, and T.I. Elington, *Distribution and sources of organic markers in artic sediments from the Mackenzie River and Beaufort shelf*, Mar. Chem. 7 (2000), pp. 23–51.
[12] K. Wyrtki, *Physical Oceanography of the Indian Ocean*, in *The Biology of the Indian Ocean*, B. Zeitzchell, ed., Springer, New York, 1973.
[13] V.V.R. Varadachari, C.S. Murthy, and V.N. Sankaranarayana, *Physical characteristics of waters and water masses off the west coast of India during late spring*, Ind. J. Mar. Science 3 (1974), pp. 1–4.
[14] S.R. Shetye, S.S.C. Shenoi, M.K. Antony, and K. Kumar, *Monthly-mean wind stress along the coast of the north Indian Ocean*, Proc. Ind. Acad. Sci. 94 (1985), pp. 129–137.
[15] S.W.A. Naqvi, D.A. Jayakumar, P.V. Narvekar, H. Naik, V.V.S.S. Sarma, S. D’Souza., Joseph, and M.D. George, *Increased marine production of N_2O due to intensifying anoxia on the Indian continental shelf*, Nature 408 (2000), pp. 346–349.
[16] S.W.A. Naqvi, H. Naik, D.A. Jayakumar, M.S. Shailaja, and P.V. Narvekar, *Seasonal oxygen deficiency over the western continental shelf of India*, in *Past and Present Water Column Anoxia*, L.N. Neretin ed., (NATO Sci. Ser. IV: Earth and Environ. Sci.; 64). Springer, Dordrecht, The Netherlands, 2006, pp. 195–224.
[17] B.R. Rao and M. Veerayya, *Influence of marginal highs on the accumulation of organic carbon along the continental slope off western India*, Deep-Sea Res. II 47 (2000), pp. 303–327.
[18] B.G. Wagle, K.H. Vora, Karisiddaiah, M. Veerayya, and F. Almeida, *Holocene submarine terraces on the western continental shelf of India; Implications for sea-level changes*, Mar. Geol. 117 (1994), pp. 207–225.
[19] D.V. Borole, *Clay sediment accumulation rates on the monsoon dominated western continental shelf and slope region of India*, Mar. Geol. 82 (1988), pp. 285–291.
[20] R.R. Nair, N.H. Hashimi, R.M. Kidwai, M.V.S. Guptha, A.L. Paropkari, N.V. Ambre, A.S. Muralinath, A. Mascarenhas, and G.P. D’Costa, *Topography and sediments of the western continental shelf of India-Vengurla to Mangalore*, Ind. J. Mar. Sci. 7 (1978), pp. 224–230.
[21] J.I. Hedges, and J.I. Stern, *Carbon and nitrogen determinations of carbonate-containing solids*, Limn. Ocean. 29 (1984), pp. 657–663.
[22] S.M. Gerchakov and P.G. Hatcher, *Improved technique for analysis of carbohydrates in sediments*, Limn. Ocean. 17 (1972), pp. 938–943.
[23] O.H. Lowry, N.J. Rosebrough, A.L. Fart, and R.J. Randall, *Protein measurement with Folin phenol reagent*, J. Biol. Chem. 193 (1971), pp. 265–275.
[24] D.L. Rice, *The detritus nitrogen problem: New observations and perspectives from organic geochemistry*, Mar. Ecol. Prog. Ser. 9 (1982), pp. 153–162.
[25] 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.
[26] W.C. Krumbein and F.J. Petti John, *Manual of sedimentary petrography*, Appleton, New York, 1938.
[27] K. Grasshoff, M. Ehrhardt, and K. Krembling, *Methods of Seawater Analysis*, Weinheim, Germany: Verlag Chemie, 1983.
[28] J.D.H. Strickland and T.R. Parsons, *A practical handbook of seawater analysis*, Bull. Fish. Res., Board Can. II Edn, 167 (1972), p. 310.

[29] H.F. Steedman, *Zooplankton Fixation and Preservation*, UNESCO Press, Paris, 1976.
[30] F.V. Banzon, R.E. Evans, H.R. Gordon, and R.M. Chomko, *SeaWiFS observation on the Arabian Sea southwest monsoon bloom for the year 2000*, Deep-Sea Res. II 51 (2004), pp. 189–208.
[31] O.M. Johannesen, G. Subbaraju, and J. Blindheim, *Seasonal variations of the oceanographic conditions off the southwest coast of India during 1971–1975*, Fisk. Dir. Skr. Ser. Hav. Under. 18 (1987), pp. 247–261.
[32] J.G. Vijay, *Nutrient dynamics in the EEZ of the west coast of India with special reference to the OMZ and denitrification*, PhD diss., Cochin University of Science and Technology, 2005.
[33] E.G. Barham, *Gaint larvacean houses: Observations from deep submersibles*, Science (1979), pp. 1129–1131.
[34] T. Ruthcastillo, Antezana, and A. Ayon, *The influence of El Nino 1997–98 on pelagic ostracods in the Humbolt current ecosystem off Peru*, Hydrobiologia 585 (2007), pp. 29–41.
[35] B. Haake, V. Ittekot, T. Rixen, V. Ramaswamy, R.R. Nair, and W.B. Curry, *Seasonality and interannual variability of particle fluxes to the deep Arabian Sea*, Deep-Sea Res. 40 (1993), pp. 1323–1344.
[36] S. Honjo, J. Dymond, W. Prell, and V. Ittekot, *Monsoon-controlled export fluxes to the interior of Arabian Sea*, Deep-Sea Res. 46 (1999), pp. 1859–1902.
[37] R.R. Nair, V. Ittekot, S.J. Manganini, V. Ramaswamy, B. Haake, and E.T. Degens, *Increased particle flux to the ocean related to the monsoons*, Nature 338 (1989), pp. 749–751.
[38] T. Rixen, B. Haake, V. Ittekot, M.V.S. Guptha, R.R. Nair, and P. Sehiuset, *Coupling between SW monsoon-related surface and deep-ocean processes as discerned from continuous particle flux measurements and correlated satellite data*, J. Geoph. Res. 101 (1996), pp. 28569–28582.
[39] T.F. Pederson and S.E. Calvert, *Anoxia vs productivity: What controls the formation of organic carbon-rich sediments and sedimentary rocks*, Am. Ass. Pet. Geol. Bull. 74 (1990), pp. 454–466.
[40] S.E. Calvert and T.F. Pederson, *Organic carbon accumulation and preservation in marine sediments: How important is the anoxia?* in *Productivity, Accumulation and Preservation of Organic Matter in Recent and Ancient Sediments*, J.K. Whelan and J.W. Farrington, eds., Columbia University Press, New York, 1992, pp. 241–263.
[41] E. Lallier-Verges, P. Bertrand, and A. Desprairies, *Organic matter composition and sulfate reduction intensity in Oman margin sediments*, Mar. Geol. 112 (1993), pp. 57–69.
[42] R.V. Tyson, *Sedimentary Organic Matter*, Chapman and Hall, London, 1995.
[43] O. Pfannkuche and K. Lochte, *The biogeochemistry of the deep Arabian Sea: Overview*, Deep-Sea Res. 47 (2000), pp. 2615–2628.
[44] R. Danovaro, D. Marrale, P. Della Croce, P. Parodi, and M. Fabiano, *Biochemical composition of sedimentary organic matter and bacterial distribution in the Aegan Sea: Trophic state and pelagic-benthic coupling*, J. Sea Res. 42 (1999), pp. 117–129.
[45] V.P. Rao and M. Lamboy, *Phosphorites from the Oman margin ODP Leg 117*, Oceanol. Acta 18 (1995), pp. 289–307.
[46] A. Suthhof, T.C Jennerjahn, P. Schaefer, and V. Ittekkot, *Nature of organic matter in surface sediments from the Pakistan continental margin and the deep Arabian Sea: Amino acids*, Deep-Sea Res. 47 (1995), pp. 329–351.
[47] R. Alagarsamy, *Organic matter composition in sediments of the Oman margin*, Chem. and Ecol. 19 (2003), pp. 419–429.
[48] K.C. Emeis, J.N. Morse, and L.L. Mays, *Organic carbon, reduced sulfur and iron in Miocene to Holocene upwelling sediments from the Oman and Benguela upwelling system*, in *Proceedings of Ocean Drilling Program Scientific Results Leg 117, College Station, TX*, W.X. Prell and N. Niitsuma, eds.,117 (1991), pp. 518–528.
[49] H.J. Smallwood, and G.A. Wolff, *Molecular characterisation of organic matter in sediments underlying the oxygen minimum zone at the Oman Marin, Arabian Sea*, Deep-Sea Res. 47 (2000), pp. 353–375.
[50] E. Kristensen, S.I. Ahmaed, and A.H. Devol, *Aerobic and anaerobic decomposition of organic matter in marine sediment: Which is fastest?* Limn. Ocean. 40 (1995), pp. 1430–1437.
[51] B. Dauwe, J.J. Middelburg, and P.M.J. Herman, *Effect of oxygen on the degradability of organic matter in subtidal and intertidal sediments of the North Sea area*, Mar. Ecol. Prog. Ser. 215 (2001), pp. 13–22.
[52] E. Kristensen, and M. Holmer, *Decomposition of plant materials in marine sediment exposed to different electron acceptors* (O_2, NO_3^- *and* SO_4^{2-})*, with emphasis on substrate origin, degradation kinetics, and the role of bioturbation*, Geochim. et Cosmochim. Acta, 65 (2001), pp. 419–433.
[53] G. Hulthe, S. Hulth, and P.O.J. Hall, *Effect of oxygen on degradation rate of refractory and labile organic matter in continental margin sediments*, Geochim. Cosmochim. Acta 62 (1998), pp. 1319–1328.
[54] G. Muri and S.G. Wakeham, *Organic matter and lipids in sediments of Lake Bled (NW Solvenia): Source and effect of anoxic and oxic depositional regimes*, Org. Geochem. 37 (2006), pp. 1649–2046.
[55] S. Prasannakumar, M. Madhupratap, M. Dileep Kumar, M. Gaune, P. M. Muraleedharan, V.V.S.S. Sarma, and S.N. de Souza, *Physical control of primary productivity on a seasonal scale in central and eastern Arabian Sea*, Proc. Ind. Acad. Sci. 109 (2000), pp. 433–441.
[56] A.A. Krishnan, P.K. Krishnakumar, and M. Rajagopalan, *Trichodesmiun erythraeum* (*Ehrenberg*) *bloom along the southwest coast of India* (*Arabian Sea*) *and its impact on trace metal concentrations in seawater*, Estuar. Coast. Shelf Sci. 71 (2007), pp. 641–646.
[57] R. Stein, *Organic carbon content/sedimentation rate relationship and its paleoenvironmental significance for marine sediments*, Geo-Mar. Lett. 10 (1990), pp. 37–44.
[58] R.G. Keil and J.I. Hedges, *Sorption of organic matter to mineral surfaces and the preservation of organic matter in coastal marine sediments*, Chem. Geol. 107 (1993), pp. 385–388.