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Intra-annual variability of carbon and nitrogen stable isotopes in suspended organic matter in waters of the western continental shelf of India

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Abstract

The $\delta^{13}C$ and $\delta^{15}N$ of water-column suspended particulate organic matter (SPOM), elemental carbon and nitrogen concentrations, and C/N ratios in SPOM, along with ancillary chemical and biological variables including phytoplankton pigment abundance, were determined every month, with the partial exception of the southwest (SW) monsoon period, from March 2007 to September 2008 at a fixed site located off Goa (central west coast of India). The results reveal significant shifts in isotopic signatures, especially $\delta^{15}N$, of SPOM before and after the onset of the SW monsoon. Very low $\delta^{15}N$ values, reaching a minimum of −4.17‰, are found during the pre-monsoon period. Although the average $\delta^{15}N$ values for the SW monsoon (6.55‰) and post-monsoon (6.19‰) are substantially higher, these values are lower than expected from a region that experiences intense water-column denitrification, as well as those reported previously from the open Arabian Sea. Our results provide the first direct evidence for the addition of substantial amounts of isotopically light nitrogen by the diazotrophs, especially *Trichodesmium*, in the region. The $\delta^{15}N$ of SPOM is generally lower than the mean value (7.38‰) for surficial sediments in the region, presumably because of diagenetic enrichment. The results support the notion that sedimentary $\delta^{15}N$ may not necessarily reflect denitrification intensity in the overlying waters due to diverse sources of nitrogen and variability of its isotopic composition. The observed intra-annual variability of $\delta^{13}C$ of SPOM is small (seasonal averages: pre-monsoon: −21.40‰, SW monsoon: −20.41‰ and post-monsoon: −22.15‰). Phytoplankton production and probably species composition could drive the observed changes. Occasional shifts in $\delta^{13}C$ toward more negative values are suggestive of terrestrial inputs, but by and large the SPOM in the region seems to be of marine origin with relatively low and constant C/N ratios (5.8–6.5) occurring throughout the study period.

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1 Introduction

Biogeochemical transformations usually involve kinetically-controlled isotopic fractions by which lighter isotopes are preferentially channeled into products with the remaining substrates becoming enriched with heavier isotopes. The stable isotopic composition of carbon and nitrogen in particulate organic matter (POM) is thus a powerful tool to investigate various transformations occurring in aquatic environments (Cifuentes et al., 1988; Bernasconi et al., 1997; Kendall et al., 2001; Huon et al., 2002; Altabet, 2006). The $^{13}C/^{12}C$ of suspended POM (SPOM) depends on the initial source of organic matter as well as various other factors such as changes in dissolved inorganic carbon (DIC), partial pressure of carbon dioxide ($p CO_2$) (Hollander and McKenzie, 1991; Rau et al., 1991; Goerike and Fry, 1994), temperature, light, pH (Thompson and Calvert, 1994), species composition (Falkowski, 1991) and food web structure (Checkley and Miller, 1989). Similarly, the $^{15}N/^{14}N$ ratio of SPOM encodes changes in water-column nitrogen cycling. For example, denitrification preferentially removes nitrate ions containing ^{14}N, leaving the residual nitrate pool enriched with ^{15}N (Naqvi et al., 1998; Brandes et al., 1998). Consequently, the $\delta^{15}N$ of organic matter photosynthesized in surface waters overlying denitrifying zones (e.g. in the Arabian Sea) is heavier than in other areas not affected by water-column denitrification (e.g. the Bay of Bengal) (Schäfer and Ittekkot, 1995; Kumar et al., 2004; Montoya and Voss, 2006). By contrast, nitrogen fixation causes minor isotopic fractionation ($\delta^{15}N$ values close to 0‰), thereby introducing isotopically lighter nitrogen into suspended organic matter (Wada et al., 1975; Saino and Hattori, 1980; Minagawa and Wada, 1986; Saino and Hattori, 1987; Carpenter et al., 1997; Altabet, 2006).

The Western Continental Shelf of India (WCSI) experiences strong intra-annual biogeochemical changes in response to monsoonal forcing. As described below, the most important feature of the oceanography of this region is the seasonal development of intense oxygen-deficiency over the shelf. This phenomenon makes the region especially sensitive and vulnerable to human-induced changes such as global warming or

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eutrophication caused by fertilizer inputs from the land (Naqvi et al., 2000, 2006a, 2006b). Indeed, it is believed that such changes may already be occurring, and that the coastal oxygen deficient system could have intensified (shifted from suboxic to anoxic) over the past few decades (Naqvi et al., 2009; and references therein). However, despite this change in the bottom-water redox conditions, sedimentary δ^{15}N, an index for water-column denitrification, shows a moderate decreasing trend during the past ~50 yr casting doubts on the fidelity of this proxy (Agnihotri et al., 2008, 2009). In order to understand the cause of this anomaly and gain insight into biogeochemical cycling of C and N, it is necessary to examine the characteristics of POM including its isotopic composition on a seasonal basis. This study makes the first such attempt in the region.

2 Methods

2.1 Study area

Time series measurements were carried out at the Candolim Time Series (CaTS) station (aka Sta. G5), which is located at Lat. 15°31′ N, Long. 73°39′ E, approximately 10 km off Candolim Beach (Goa), central west coast of India (Fig. 1). The mean water depth at this site is ~27 m (Fig. 1).

Circulation at the study site, as in the entire Indian Ocean Arabian Sea, undergoes semi-annual reversals associated with the monsoons (Schott and McCreary, 2001). The southwest (SW) monsoon is particularly strong in this area. During this time (from May to October) the surface current (the West India Coastal Current, WICC) flows southward, inducing moderate upwelling along the coast, which enriches the euphotic zone with nutrients. Although the northeast (NE) monsoon is less intense, the associated surface circulation is anomalously strong. During this period (from December to March) the WICC is directed northward, opposing the wind, and the WCSI experiences downwelling and relatively oligotrophic conditions. As a consequence of the

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alternating upwelling and downwelling regimes, the WCSI experiences extreme variability of biogeochemical cycling. Of particular interest is the aforementioned seasonal occurrence of widespread and intense oxygen deficiency, which is associated only with the SW monsoon circulation. Three factors contribute to the development and sustenance of this phenomenon: (1) the initial oxygen content of upwelling waters is low; (2) the upwelled water gets stagnated over the shelf, in part due to weak upwelling and in part because it gets capped by a thin (5–10 m) fresher-water lens formed as a result of intense rainfall in the coastal zone; and (3) moderate biological production largely sustained by the upwelled nutrients supports fairly high respiration rates in subsurface waters. The subsurface waters lose all dissolved oxygen by July/August, thus allowing heterotrophic bacteria to respire using nitrate, converting it to molecular nitrogen and nitrous oxide (denitrification). As the nitrate brought up by the upwelled water gets exhausted, usually by September/October, sulphate reduction sets in, manifested by the appearance of hydrogen sulphide and the accumulation of ammonium in bottom waters (Naqvi et al., 2000, 2006a, 2006b). Oxic conditions are restored with the reversal of WICC sometime in November. The shallow oxygen-deficient zone that develops seasonally over the WCSI is the largest of its kind in the world. As stated above, although formed essentially due to natural processes, this systems appeared to have been substantially impacted by human activities (Naqvi et al., 2009; and references therein).

2.2 Sampling

Samples for elemental and isotopic analyses of SPOM were collected during March 2007–September 2008 covering almost all months except June–August 2007 and June–July 2008 when the sea was too rough to visit the site with the boats available to us. Niskin samplers (5-l) mounted on nylon ropes and fitted with reversing thermometers were used for the sampling. Samples were also collected for routine biological and chemical core measurements that were made following standard procedures (JGOFS, 1991). Subsamples for the SPOM were immediately transferred to acid-cleaned plastic carboys and taken to the laboratory within 2 h of collection where they were filtered without any further delay through 0.7 µm pore size Whatmam GF/F filters precombusted at 450 °C for 4 h. The filters were decalcified by exposing to fumes of HCl (37%) for 12 h in a desiccator, dried and packed tightly in tin cups for analysis of isotopic ratios. Stable carbon and nitrogen isotope ratios were measured using a Thermo Finnigan DELTA V plus isotope ratio mass spectrometer in continuous-flow mode after high temperature flash combustion at 1050°C in a EURO3000 Eurovector elemental analyzer (Owens and Rees, 1989). The ratios are expressed in per mil notation as follows:

$$\delta^{15}\text{N or } \delta^{13}\text{C}(‰) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000, \quad \text{where } R = {}^{15}\text{N}/{}^{14}\text{N or } {}^{13}\text{C}/{}^{12}\text{C} \qquad (1)$$

with the standards being atmospheric N_2 and Pee Dee Belemnite (PDB), respectively.

Reference tanks for N and C isotopes were filled with N_2 (99.9995%) and CO_2(99.995%). The N_2 was calibrated against an IAEA standard, while a working standard, ε-Amino-n-Caproic Acid (ACA), kindly supplied by Prof. Mark Altabet of School for Marine Sciences and Technology (SMAST), University of Massachusetts-Dartmouth, USA, was run to check the precision. Reported ACA values of $\delta^{15}N$ and $\delta^{13}C$ are 4.6‰ and −25.3‰ respectively. Standard deviation for both $\delta^{13}C$ and $\delta^{15}N$ was less than 0.2‰.

2.3 Pigment analysis

For the pigment analysis, 1–2 l of water sample was immediately filtered using a GF/F filter (pore size 0.7 µm) avoiding exposure to direct light. The filter paper was stored in liquid nitrogen until analysis in the shore laboratory. Phytoplankton pigments from the frozen filter were extracted into 3 ml of 95% acetone (v/v in deionized water) for 5 min using an ultrasonic bath (5 s, 20 kHz) filled with ice-water. The extract was stored overnight at −20 °C for high performance liquid chromatography (HPLC) analysis. The extract was passed through a Teflon syringe cartridge (Millipore) having a glass fiber pre acrodisc filter (pore size 0.45 µm, diameter 25 mm) to remove all cellular

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debris. The clear extract was then collected in a 5 ml glass vial and placed directly into the temperature controlled (5 °C) auto-sampler tray for HPLC analysis. The entire extraction procedure was carried out in dim light conditions and at low temperature to minimize degradation of pigments. The HPLC analysis was carried out following the method of Van Heukelem (2002) as detailed in Roy et al. (2006). The sum of 19′-hexanoyloxyfucoxanthin (19′HF), 19′-butanoyloxyfucoxanthin (19′BF), Alloxanthin (Allo) and Chlorophyll-*b* was used to indicate the abundance of nanoflagellates. Zeaxanthin (Zea), Fucoxanthin (Fuco) and Peridinin (Per) were considered to represent cyanobacteria, diatoms and dinoflagellates, respectively.

3 Results

Distributions of dissolved oxygen (O_2), nitrate (NO_3^-) and (chlorophyll-*a*) with depth and time at the CaTS site during the period of the study are shown in Fig. 2. The observed variations of the C and N contents, C/N ratios, $\delta^{13}C$ and $\delta^{15}N$ at the CaTS location are shown in Fig. 3, while the corresponding data on various biomarker pigments are plotted in Fig. 4. The arithmetic means of the variables for the four depths sampled (surface, 9 m, 18 m and 27 m) are also included in Fig. 3 and Fig. 4 connected by the bold blue lines passing through the bars. The results have been grouped according to three seasons, i.e. pre-monsoon, SW monsoon and post-monsoon.

3.1 Pre-monsoon/summer (late February–May)

The water-column was generally well-mixed, oxygenated and nutrient-impoverished during the pre-monsoon periods (Fig. 2a). Dissolved O_2 and NO_3^- concentrations averaged 177 µM ($n = 40$, SD ± 47) and 1.07 µM ($n = 41$, SD ± 2.18), respectively. However, the near-bottom waters were observed to lose O_2 and accumulate NO_3^- toward the end of the season, especially in 2008. The chlorophyll-*a* concentration was generally low, averaging 411 ng l^{-1} ($n = 34$, SD ± 370).

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The $\delta^{13}C_{SPOM}$ and $\delta^{15}N_{SPOM}$ averaged −21.40‰ ($n = 40$, SD ± 1.18‰) and 2.69‰ ($n = 41$, SD ± 3.14‰), respectively. The overall depthwise distribution of $\delta^{13}C$ did not show any significant variation between surface and bottom waters. By contrast, $\delta^{15}N$ showed a significant depletion from surface to bottom waters, with the values averaging 3.80‰ at the upper two depths (0 and 9 m), 1.52‰ at 18 m, and 0.97‰ close to the bottom. The C/N ratios showed a mean of 5.94 ($n = 41$, SD ± 1.66). A comparison of $\delta^{13}C$ with the total chlorophyll-*a*, showed a good positive correlation of 0.68 (Fig. 5a) whereas a very poor correlation ($r^2 = 0.17$) was observed between $\delta^{13}C$ and $\delta^{15}N$ (Fig. 5b). The carbon content of SPOM averaged 22.0 µM ($n = 41$, SD ± 16.0) ranging widely from 8.1 µM to 81.4 µM with higher values observed mostly in bottom waters. The nitrogen content varied over a narrow range (1.4–8.9 µM) with an average of 3.5 µM ($n = 41$, SD ± 1.7). The lowest values were observed during the first week of April 2008. A comparison of average water-column $\delta^{13}C_{SPOM}$ with that for the underlying surface sediments (−21.03‰) showed only 0.37‰ difference, but this was not the case with $\delta^{15}N$, which was much lower (by 4.69‰) in the water-column SPOM relative to surface sediments (averaging 7.38‰).

3.2 SW monsoon (June–September)

The dissolved O_2 concentration averaged 126 µM ($n = 10$, SD ± 85) with the O_2 levels in the bottom waters falling sharply, triggering the onset of suboxic conditions. The average NO_3^- concentration increased to 3.03 µM ($n = 11$, SD ± 4.10), as also did the phytoplankton biomass as indicated by the chlorophyll-*a* the concentration of which averaged 1169 ng l^{-1} ($n = 8$, SD ± 1005).

The $\delta^{13}C$ of SPOM during the SW monsoon averaged −20.41‰ ($n = 10$, SD ± 2.99‰), not differing significantly from the pre-monsoon value. By contrast, the $\delta^{15}N$ showed an overall enrichment to 6.55‰ ($n = 11$, SD ± 2.51‰). Also, unlike the pre-monsoon, when there was no significant depthwise trend in $\delta^{13}C$ distribution, an enrichment by −2.2‰ was seen in bottom waters as compared to surface waters during

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SW monsoon. On the other hand, while the $\delta^{15}N$ had shown a significant decrease from surface to bottom waters during pre-monsoon, such a trend was not observed during SW monsoon. The $\delta^{13}C$ showed a good positive correlation with $\delta^{15}N$ ($r^2 = 0.61$, Fig. 5c). The C/N ratio averaged 5.77 ($n = 11$, SD ± 0.96), slightly higher than the corresponding pre-monsoon values. The carbon content varied from 13.1 µM to 62.2 µM with an average of 31.8 µM ($n = 11$, SD ± 14.7). The nitrogen content fluctuated from 2.5 µM to 8.7 µM; the overall average of 5.6 µM ($n = 11$, SD ± 2.5) was higher by 2 µM than that observed during pre-monsoon. Unlike the pre-monsoon, the average value of $\delta^{15}N_{SPOM}$ was close to that in the underlying surficial sediments, showing only a minor (0.8‰) depletion.

3.3 Post-monsoon (October–January)

Well-oxygenated conditions prevailed in the entire water-column, barring the near-bottom waters early during the season, with an average O_2 concentration of 177 µM ($n = 14$, SD ± 38). Nitrate levels decreased to an average of 0.68 µM ($n = 16$, SD ± 0.80) with the exception of a high value observed on 10 November 2007 at 27 m. The chlorophyll-*a* concentrations were moderate, averaging 844 ng l^{-1} ($n = 8$, SD ± 393).

The $\delta^{13}C$ and $\delta^{15}N$ values averaged −22.15‰ ($n = 16$, SD ± 2.08‰) and 6.19‰ ($n = 16$, SD ± 1.70‰), respectively. The shift from SW monsoon to post-monsoon did not cause any large change in isotopic values, although $\delta^{13}C$ did decrease by 1.7‰ during post-monsoon. The vertical distribution of $\delta^{13}C$ was characterized by slightly less negative values (average −21.5‰) than the bottom water (average −22.7‰). Such a trend was absent in the water-column distribution of $\delta^{15}N$. The $\delta^{13}C$ and $\delta^{15}N$ did not show any significant correlation (Fig. 5f). On an average the C/N ratios (6.55 ± 1.39‰, $n = 16$), were much higher than those recorded during the pre-monsoon (5.94) and SW monsoon (5.77) seasons. The carbon content varied from 13.0 µM to 39.0 µM, averaging 21.6 µM ($n = 16$, SD ± 7.6). The nitrogen content ranged from 1.9 µM to

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6.7 µM with an overall average of 3.4 µM ($n = 16$, SD ± 1.2). On average, the lowest nitrogen content was observed during pre-monsoon (3.4 µM). While the average N content decreased from the SW monsoon maximum (5.6 µM) by 2.2 µM in post-monsoon, the δ^{15}N underwent only a slight change, decreasing by 0.36‰. As compared to δ^{15}N, the seasonal changes observed in average δ^{13}C were quite small (pre-monsoon: −21.40‰, SW monsoon: −20.41‰ and post-monsoon: −22.15‰).

4 Discussion

As described in Sect. 2.1, the WCSI experiences a variety of physico-chemical conditions that seem to modulate carbon and nitrogen cycling as well as their isotopic signatures in SPOM. The most important physico-chemical phenomenon occurring in the region is the alternating upwelling and downwelling related suboxic/anoxic and oxic conditions in near-bottom waters, each lasting for several months, the former from July/August to October/November and the latter during the rest of the year. In this section we relate these water-column transformations to the isotopic composition on SPOM.

4.1 Pre-monsoon

During the pre-monsoon/summer season the water-column at the study site remains well oxygenated (Fig. 2a). Nutrient concentrations are generally low (e.g. NO_3^-, NO_2^-, and ammonium (NH_4^+) values being in the ranges 1–4 µM, 0.5–1 µM and 0–1 µM, respectively; Naqvi et al., 2006a). Toward the end of the pre-monsoon season, however, O_2 depletion and associated nutrient enrichment may sometimes occur in near-bottom waters due to an early onset of upwelling as evident by the high NO_3^- concentration recorded by us at 27 m on 24 May 2007 (Fig. 2b). The δ^{15}N of SPOM during this season was found to fluctuate widely, from 7.50‰ to −4.17‰. Values at the lower end of this range are not commonly observed in tropical waters but comparable δ^{15}N data

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(−4‰ to −5‰) have been reported from the high-nutrient, low chlorophyll (HNLC) regions such as the Southern Ocean (Altabet and Francois, 1994, 2001). We carried out frequent sampling during pre-monsoon of 2008 (on 8 field trips between 27 February and 8 May) to investigate N isotopic shifts occurring during this season. Following the maximum observed during the SW monsoon-post-monsoon periods, discussed in the following sections, the δ^{15}N of SPOM decreased to ~4‰ at the beginning of the pre-monsoon season, well below the δ^{15}N of SPOM reported from the open-ocean surface waters of the Arabian Sea (Montoya and Voss, 2006). This decrease is apparently caused by a shift in the type and/or isotopic composition of the nitrogenous nutrients used by the phytoplankton. However, a more rapid decrease in δ^{15}N occurred between 5 and 13 March to values as low as −4.17‰. On the latter occasion, as also on two subsequent trips to the CaTS site, we observed large vertical gradients with the δ^{15}N values decreasing with depth. With the exception of the surface value on 27 March, the δ^{15}N was consistently lower than 2‰ during this period. Such low values can only be caused by N_2 fixation. Blooms of nitrogen fixing *Tricodesmium* are known to occur in Indian coastal waters at this time of the year (Devassy et al., 1978). From the data collected in the present study it would appear that the bloom formation began by the end February 2008 (when minute spores appeared in water), peaked around 13 March (as inferred from the minimum δ^{15}N) and then decayed in the following weeks as evident from the increase in δ^{15}N by ~3.8‰. The increase in δ^{15}N during the later half, i.e. the declining phase of the bloom, indicates gradual removal of isotopically lighter nitrogen and/or inputs of isotopically heavier new nitrogen from other sources (e.g. from the sediments as the shallow water-column is well-mixed during this period). Nevertheless, the δ^{15}N values remained fairly depressed during the three visits to the CaTS site in April and May 2008. The surface-water NO_3^- concentration remained low (<1 µM) throughout this bloom. Surprisingly, despite the lower δ^{15}N, there was not much accumulation of either POC or PON, with the PON varying within a narrow range of 2–5 µM. It may be pointed out that while the pre-monsoon season is indeed a time of high N_2 fixation, the intensity of the process probably varies substantially from year to year. The blooms

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could also be patchy in space and time. Thus, in 2007 low $\delta^{15}N$ values were encountered only on the last of the three samplings carried out from 30 March to 24 May. The preponderance of N_2-fixing cyanobacteria during March 2008 is supported by data on the marker pigment Zeaxanthin, which was found to be as high as 27.4 ng l^{-1}. Previous studies at this location by Roy et al. (2006) and Roy (2010) had also shown that the pre-monsoon season is dominated by cyanobacteria of the genus *Trichodesmium.*

The $\delta^{13}C$ of SPOM varied over a narrow range (−22.96‰ to −19.65‰) except for a few lighter values (∼−24‰) observed in 2007 and also at the surface on 2 April 2008. Thus, the organic matter at this site during the pre-monsoon season bears mostly the marine signature i.e., $\delta^{13}C = -18$‰ to −24‰ (Fry and Scherr, 1984; Riera et al., 1999; Darnaude et al., 2004). The growth and decay of *Trichodesmium* were accompanied by a prominent change in $\delta^{15}N$, but did not have any significant effect on $\delta^{13}C$. A good positive correlation ($r^2 = 0.68$) between chlorophyll-*a* and $\delta^{13}C$ (Fig. 5a) indicates that the observed carbon isotopic fractionation is largely due to the uptake of CO_2 by phytoplankton. The C/N ratios are indicative of the source of the organic matter. For the material synthesized by the phytoplankton these ratios range from 6 to 9 (Holligan et al., 1984), whereas terrestrial organic matter is characterized by higher C/N (>12) (Hedges and Mann, 1979). As the average C/N ratio observed during pre-monsoon is 5.95, it further contributes to the conclusion that the SPOM is largely marine (Redfield et al. 1963). Further, as this ratio is lower than the Redfield value (6.6), it would seem that N_2-fixing *Trichodesmium*, which appear to have somewhat lower C/N (Carpenter et al., 2004) may to a large extent be involved in its synthesis. A comparison of the $\delta^{13}C$ of SPOM in the water-column with that of the underlying surface sediments (−21.03‰) showed only a 0.37‰ difference.

4.2 SW monsoon

Unfortunately, as stated earlier, we could not carry out any sampling during the months of June–August in 2007 and June–July in 2008 due to bad weather, and so the data

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presented here only come from September 2007 and August 2008 onwards, representing the latter part of the SW monsoon. The data for the two years are somewhat divergent in that the September 2007 measurements yielded low (<4‰) δ^{15}N values, whereas the 2008 values are among the highest observed during the entire study period, reaching as high as ~10‰ at the surface on 27 August. The δ^{15}N on this occasion decreased with depth, a trend that reversed the next month. The high values can be easily explained by the uptake by phytoplankton from a pool of heavier nitrate created by denitrification. However, the available data on nitrogen isotopic composition of nitrate from coastal waters off western India during the late SW monsoon shows huge variability (δ^{15}N = 3.7–22.5‰) (Naqvi et al., 2006). It is hard to pin down the cause of the surprisingly low δ^{15}N values, although several possibilities have been suggested (Naqvi et al., 2006). However, irrespective of the cause, the uptake of lighter nitrate could have led to the low δ^{15}N of SPOM measured by us in September 2007. The other alternative is that the source of nitrogen also could have been different (possibly ammonium produced during the anoxic decay of organic matter). It may be noted that during the periods of complete anoxic (sulphidic) conditions ammonium is the dominant source of nitrogen even for the new production by the phytoplankton (Naqvi et al., 2006). In any case, results of previous studies as well as those being reported here suggest a complex and dynamic system with large variability in the sources and isotopic composition of nitrogen available for phytoplankton uptake and of the organic matter produced by them.

The δ^{13}C of SPOM generally ranged from −17.6 to −19.7‰, and was thus typically of marine origin. The modest enrichment of ^{13}C in SPOM during the SW monsoon (i.e. the relatively less negative values) as compared to pre-monsoon may be attributed to the dominance of diatoms and dinoflagellates. The presence of these large-celled phytoplankton is supported by prominent increases in their respective marker pigments – Fucoxanthin (72.8 ng l^{-1}) and Peridinin (22 ng l^{-1}), respectively. Thus, there occurred a shift in phytoplankton species composition from pre-monsoon to SW monsoon that could possibly affect δ^{13}C of SPOM, as different phytoplankton groups have

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different isotopic fractionation factors (Falkowski, 1991). ^{13}C depletion to around −26‰ in the surface and sub-surface (9 m) waters was observed on 30 September 2007. While such depletion is characteristic of terrestrial organic matter, the corresponding C/N value (5.7) is not indicative of the terrestrial origin. We are unable to explain this anomaly. A fairly good linear correlation was observed between δ^{13}C and δ^{15}N ($r^2 = 0.61$, Fig. 5c) during the SW monsoon. However, this seems to be determined largely by the two values with very negative δ^{13}C as well as relatively low δ^{15}N; apparently these samples were affected by terrestrial inputs. There also exists a significant correlation between δ^{15}N and PON ($r^2 = 0.56$, Fig. 5d) suggesting that high production occurs when isotopically heavier nitrogen is available for phytoplankton growth. It could also be due to isotopic fractionation during the formation of PON. The δ^{13}C versus POC plot shows a great deal of scatter and consequently a poor correlation ($r^2 = 0.37$, Fig. 5e) despite the two low δ^{13}C values referred to above.

4.3 Post-monsoon

The effects of SW monsoon spill over to, and indeed are sometimes more intense, during the early (October–November) post-monsoon period in terms of severe anoxia. Thus, similar to the conditions encountered during the late SW monsoon of 2008 and presumably driven by the same process (denitrification), enrichment of ^{15}N in SPOM to a maximum of 8.15‰ was noticed on 10 November 2007; also, there occurred a decrease by 2.5‰ in δ^{15}N in bottom waters as compared to the surface and sub surface waters with corresponding sharp increase in NO_3^- concentrations by 2.8 µM and accompanied by fall in O_2 concentration by 110 µM. The δ^{15}N decreased thereafter and fluctuated between 3.60‰ and 7.39‰ from 4 December to 31 January 2008. After the termination of upwelling and associated anoxic conditions, other diverse sources of nitrogen to coastal waters including sedimentary inputs and deposition of largely anthropogenic nitrogen from the atmosphere, which is maximal during the winter (Duce et al., 2008), could account for the observed variations.

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The SPOM became progressively more enriched with ^{13}C from 10 November to 28 December 2008 (depth-averaged $\delta^{13}C$ increasing from −23.68‰ to −19.26‰). With the C/N ratio hovering around 6, close to the Redfield value, the organic matter was predominantly of marine origin. The sampling on 31 January, however, yielded much lighter values (to around −27‰ in the near-bottom water) with an overall average of −24.74‰. This suggests the predominance of terrestrial organic matter, which is further supported by a high C/N ratio (8.3). On the average the $\delta^{13}C$ during post-monsoon was slightly depleted than the pre-monsoon and SW monsoon values, indicating greater contribution by terrestrial organic matter. Alternatively, the observed change could also arise from a different phytoplankton species composition during the post- monsoon period. Although the pigment data from our study are not sufficient to show this change, Roy (2010) reported the abundance of smaller phytoplankton groups like nanoflagellates dominated by prymnesiophytes and green algae during this period.

5 Summary and conclusions

It is for the first time that the natural abundance of stable C and N isotopes in SPOM has been used as a tool to study biogeochemical processes over the western continental shelf of India, a region of global significance on account of being the largest natural seasonally-occurring coastal oxygen-deficient zone in the world with large efflux of N_2O to the atmosphere. The results reveal large intra-annual variations in $\delta^{15}N$ of SPOM probably driven by a combination of diverse sources of nitrogen (upwelling, sedimentary inputs, atmospheric deposition and land runoff) as well as biological processes especially nitrogen fixation, nitrification, nitrogen assimilation and denitrification. The most prominent changes occurred before and during/slightly after the SW monsoon. The progressive development of the *Trichodesmium* blooms, which is a regular feature in warm oligotrophic waters, significantly lowers the $\delta^{15}N$ of SPOM during the pre-monsoon season, whereas water-column denitrification makes SPOM enriched in $\delta^{15}N$ during the late SW monsoon. Another important result of the present study is that

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the δ^{15}N of SPOM is generally lower than the mean value (7.38‰) for surficial sediments. However, the moderately high sedimentary δ^{15}N value still does not reflect the intensity of seasonal denitrification in the overlying waters. These results imply limited utility of sedimentary δ^{15}N as a water-column denitrification proxy in the region.

The amplitude of the δ^{13}C variability in SPOM is relatively small. Phytoplankton production and probably species composition could account for the observed δ^{13}C changes. Occasional shifts in δ^{13}C toward more negative values are suggestive of terrestrial inputs, but by and large the SPOM in the region is mostly of marine origin with relatively low and constant C/N ratio throughout the study period.

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Table 1. Isotopic values ($\delta^{13}C$ and $\delta^{15}N$) of SPOM, their elemental C and N concentrations µM), C/N ratios, O_2, NO_3^- and phytoplankton pigment abundance ($ng\,l^{-1}$) during pre-monsoon season at G5 station in the WCMI.

Date	Depth (m)	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	C	N	C/N	O_2	NO_3	Zea*	Fuco*	Per*	19′HF + 19′BF*	Chl-*b* + Lutein*	Allo*	TChl-*a**
30 Mar 07	0	−23.78	7.47	27.2	3.2	8.42	256	0	3	2	1	1	0	1	18
5 Apr 2007	0	−22.96	7.01	81.4	8.9	9.15	268	2.79	7	2	5	2	3	0	35
	9	−21.81	7.50	48.6	6.6	7.41	270	0.51	2	3	2	1	2	0	27
	18	−22.74	6.69	64.2	6.4	9.99	198	0.26	1	9	4	1	2	1	27
	27	−23.60	5.15	54.8	6.0	9.20	111	2.64	3	11	4	1	2	1	32
24 May 2007	0	−23.83	1.21	16.7	4.2	3.97	207	0.95							
	9	−21.53	3.23	33.1	4.8	6.89	201	1.06	5	14	2	1	3	1	96
	18	−19.65	−2.44	19.9	4.0	4.95	79	4.80	4	6	5	2	3	1	86
	27	−19.91	−4.17	43.8	8.4	5.21	55	9.94	4	14	8	1	2	2	153
27 Feb 2008	0	−20.82	4.28	15.9	3.0	5.26	201	1.00	46	71	9	1	16	11	764
	9	−20.27	3.49	16.2	3.1	5.18	201	0.97	57	70	27	1	13	9	741
	18	−21.15	4.58	13.8	2.2	6.41	192	1.43	28	55	6	0	17	8	593
	27	−21.51	4.19	14.7	2.8	5.30	185	2.32							
5 Mar 2008	0	−21.08	4.37	11.7	2.7	4.39	203	0.02	52	20	11	3	8	2	342
	9	−21.21	3.99	9.9	2.1	4.75	197	0.01	26	58	7	2	8	3	492
	18	−20.72	3.06	9.6	2.4	4.06	188	0.19	26	60	4	2	6	4	472
	27	−19.72	1.95	12.2	2.7	4.60	185	0.27	24	160	5	2	6	3	1094
13 Mar 2008	0	−21.33	1.29	13.8	3.2	4.26	197	0.01	41	10	4	4	4	3	239
	9	−21.97	−0.40	10.8	2.6	4.19	198	0.00	41	3	0	3	6	1	150
	18	−22.15	−2.03	8.7	2.4	3.68	196	0.00						1	
	27	−21.23	−3.77	7.9	2.3	3.45	153	0.92	32	5	4	5	7		202
19 Mar 2008	0	−19.77	1.92	19.7	3.1	6.46	124	0.01	46	56	84	5	19	6	684
	9	−19.84	1.65	16.9	3.0	5.64		0.00	51	35	9	12	11	3	641
	18		1.65	21.0	3.3	6.42	208	0.09	6	66	3	0	5	3	456
	27	−21.01	−1.01	40.8	4.7	8.76	176	0.67	13	143	0	0	9	6	1112
27 Mar 2008	0	−20.94	6.23	19.5	3.2	6.07	198	0.32	103	102	18	4	10	5	980
	9	−20.78	1.31	16.5	3.7	4.50	199	0.10	79	104	13	7	17	5	1012
	18	−20.79	−3.58	18.5	3.7	5.02	198	0.10	40	56	0	2	8	1	479
	27	−20.22	0.07	23.1	3.9	5.90	187	0.35	52	70	0	0	7	3	573
2 Apr 2008	0	−24.29	6.84	20.4	2.1	9.67	198	0.02	7	18	49	8	4	1	171
	9	−22.77	5.29	9.2	1.3	7.21	199	0.00	10	20	3	2	14	2	165
	18	−21.74	2.78	9.7	1.4	6.73	204	0.04	12	23	3	0	12	1	182
	27	−21.25	2.70	8.1	1.4	5.75	172	0.35	8	25	1	1	8	1	230
30 Apr 2008	0	−21.93	−1.63	10.9	1.9	5.85	139	0.14	18	3	0	1	4	1	96
	9	−21.74	5.15	20.5	3.7	5.52	138	0.00	22	7	9	2	15	1	123
	18	−22.01	2.76	10.4	2.0	5.13	141	0.00	28	6	0	4	9	1	178
	27	−20.86	2.58	26.7	4.8	5.57	81	1.78	34	163	11	3	11	1	1334
8 May 2008	0	−20.11	4.65	16.0	2.8	5.63	175	0.01	No Data	No Data	No Data	No Data	No Data	No Data	No Data
	9	−20.35	5.03	19.3	3.6	5.40	147	0.10							
	18	−21.22	4.20	17.5	3.5	5.02	159	0.68							
	27	−21.32	5.11	22.6	3.4	6.62	101	9.16							
Mean		−21.40	2.69	22.0	3.5	5.94	177	1.07	27.4	43.2	9.2	2.5	8.0	2.7	411
SD ±		1.18	3.14	16.0	1.7	1.66	47	2.18	24.0	46.1	16.2	2.6	5.1	2.6	370

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Table 2. Isotopic values (δ^{13}Cand δ^{15}N) of SPOM, their elemental C and N concentrations µM), C/N ratios, O_2, NO_3^- and phytoplankton pigment abundance (ng l^{-1}) during SW monsoon season at G5 station in the WCMI.

Date	Depth (m)	δ^{13}C ‰	δ^{15}N ‰	C	N	C/N	O_2	NO_3	Zea*	Fuco*	Per*	19′HF + 19′BF*	Chl-*b* + Lutein*	Allo*	TChl-*a**
30 Sep 2007	0	−25.11	4.07	15.8	2.5	6.40	218	2.29	27	19	5	5	22	3	239
	9	−26.74	2.19	13.1	2.7	4.88	164	0.26	14	23	18	4	14	4	287
	18		3.64	16.7	2.9	5.69	26	1.98	12	46	5	3	8	2	301
	27						3	0.80	17	107	22	2	11	3	684
27 Aug 2008	0	−19.74	10.43	34.5	6.0	5.72	187	0.23	72	139	51	23	51	3	2634
	9	−19.05	9.90	47.4	10.2	4.66	187	5.20	65	96	52	0	90	12	2675
	18	−19.11	7.69	39.9	7.3	5.45	8	10.34	22	90	23	4	15	10	1218
	27	−19.72	6.22	62.2	8.5	7.31		11.16	13	62	0	0	17	3	1313
9 Sep 2008	0	−19.38	6.32	32.4	4.3	7.62	199	0.10	No Data	No Data	No Data	No Data	No Data	No Data	No Data
	9	−17.64	7.05	30.3	5.6	5.37									
	18	−18.98	7.05	23.7	4.4	5.45	171	0.10							
	27	−18.67	7.50	34.2	6.9	4.97	99	0.90							
Mean		−20.41	6.55	31.8	5.6	5.77	126	3.03	30.3	72.8	22.0	5.1	28.5	5.0	1169
SD ±		2.99	2.51	14.7	2.5	0.96	85	4.10	24.2	42.4	20.1	7.5	28.2	3.8	1005

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Table 3. Isotopic values ($\delta^{13}C$ and $\delta^{15}N$) of SPOM, their elemental C and N concentrations µM), C/N ratios, O_2, NO_3^- and phytoplankton pigment abundance ($ng\,l^{-1}$) during post-monsoon season at G5 station in the WCMI.

Date	Depth (m)	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	C	N	C/N	O_2	NO_3	Zea*	Fuco*	Per*	19′HF + 19′BF*	Chl-*b* + Lutein*	Allo*	TChl-*a**
10 Nov 2007	0	−22.24	8.14	23.0	3.2	7.22	202	0.26	No	No	No	No	No	No	No
	9	−22.29	9.26	17.3	3.0	5.79	174	0.70	Data	Data	Data	Data	Data	Data	Data
	18	−23.68	8.91	10.4	1.8	5.95	173	0.78							
	27	−22.89	6.30	24.9	5.0	4.99	73	3.38							
4 Dec 2007	0	−20.17	5.21	39.0	6.7	5.79	201	0.46	71	141	18	1	56	6	1454
	9	−18.97	3.60	16.9	3.0	5.63	191	0.37	64	99	8	1	7	4	707
	18	−21.44	5.09	17.9	3.5	5.06	183	0.34	18	66	2	0	4	2	410
	27	−21.8	4.04	13.0	1.9	6.69	118	0.49	10	48	0	1	3	2	244
28 Dec 2007	0	−20.70	7.33	22.6	3.9	5.81	203	1.64	1	83	9	3	12	8	1060
	9	−20.71	5.66	19.6	3.5	5.61	186	0.34	1	65	53	2	15	2	934
	18	−20.79	7.39	17.5	2.9	6.07	181	0.50	1	109	3	3	17	4	1134
	27	−19.82	6.96	15.4	2.2	7.00	177	0.51	1	73	0	2	10	1	809
31 Jan 2008	0	−24.00	4.24	20.1	2.6	7.66		0.13	No	No	No	No	No	No	No
	9	−22.70	4.95	23.7	3.3	7.24	214	0.31	Data	Data	Data	Data	Data	Data	Data
	18	−25.52	5.68	34.7	4.5	7.66	208	0.20							
	27	−26.72	6.27	29.4	2.8	10.66		0.54							
Mean		−22.15	6.19	21.6	3.4	6.55	177	0.68	20.9	85.5	11.6	1.6	15.5	3.6	844
SD ±		2.08	1.70	7.6	1.2	1.39	38	0.80	29.5	29.7	17.8	1.1	17.1	2.4	393

* Zeaxanthin (Zea), Fucoxanthin (Fuco), Peridinin (Per), 19'-hexanoyloxyfucoxanthin (19′HF), 19′-butanoyloxyfucoxanthin (19′BF), Alloxanthin (Allo), Chlorophyll-*b* + lutein (Chl *b* + lutein) and Total Chlorophyll-*a* (TChl *a*).

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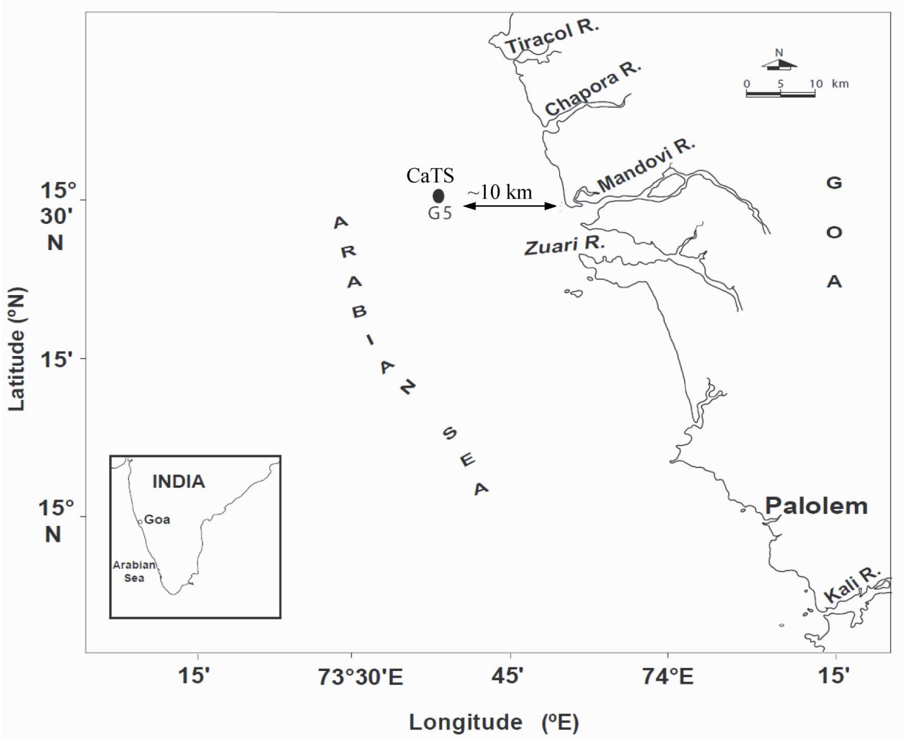

Fig. 1. Map of the study area showing the location of Candolim Time Series (CaTS) station (G5) off Goa.

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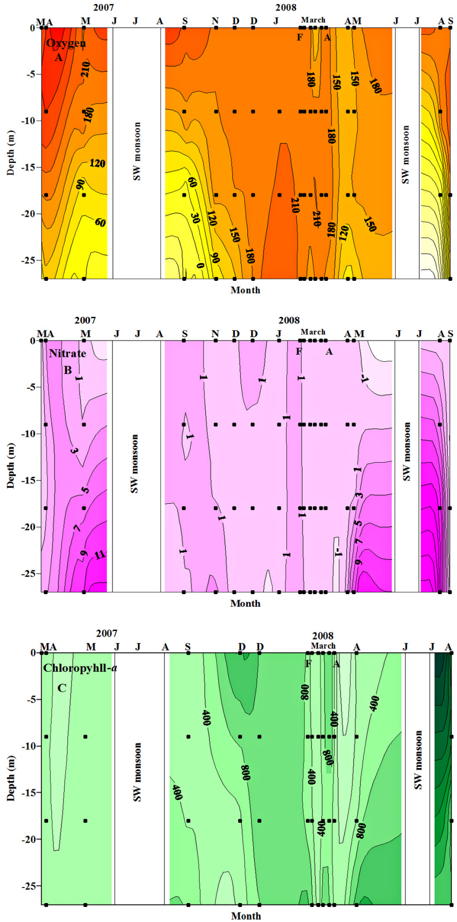

Fig. 2. Variations with depth and time in dissolved O_2 **(A)**, nitrate **(B)** and chlorophyll-*a* **(C)** at the CaTS site from March 2007 to September 2008. Note that observations could not be made during the SW monsoon due to rough weather.

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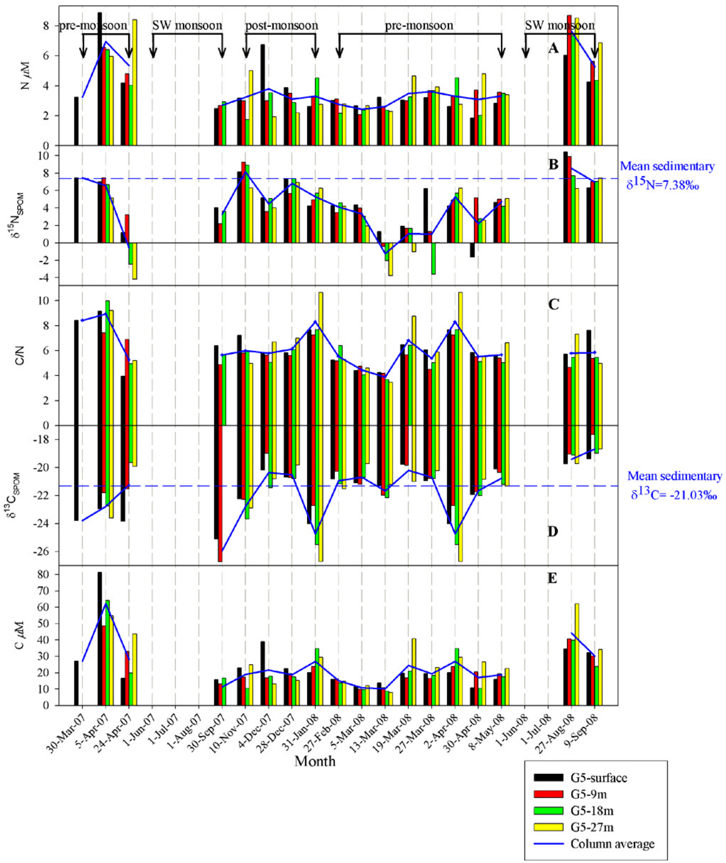

Fig. 3. Intra-annual variations of elemental nitrogen concentration **(A)**, δ^{15}N **(B)**, C/N **(C)**, δ^{13}C **(D)** and carbon concentration **(E)** in SPOM at the CaTS site from March 2007 to September 2008. The three seasons (pre-monsoon, SW monsoon and post-monsoon) are marked in the figure. The bold blue line represents column-averaged values (0 m, 9 m, 18 m and 27 m) for each parameter.

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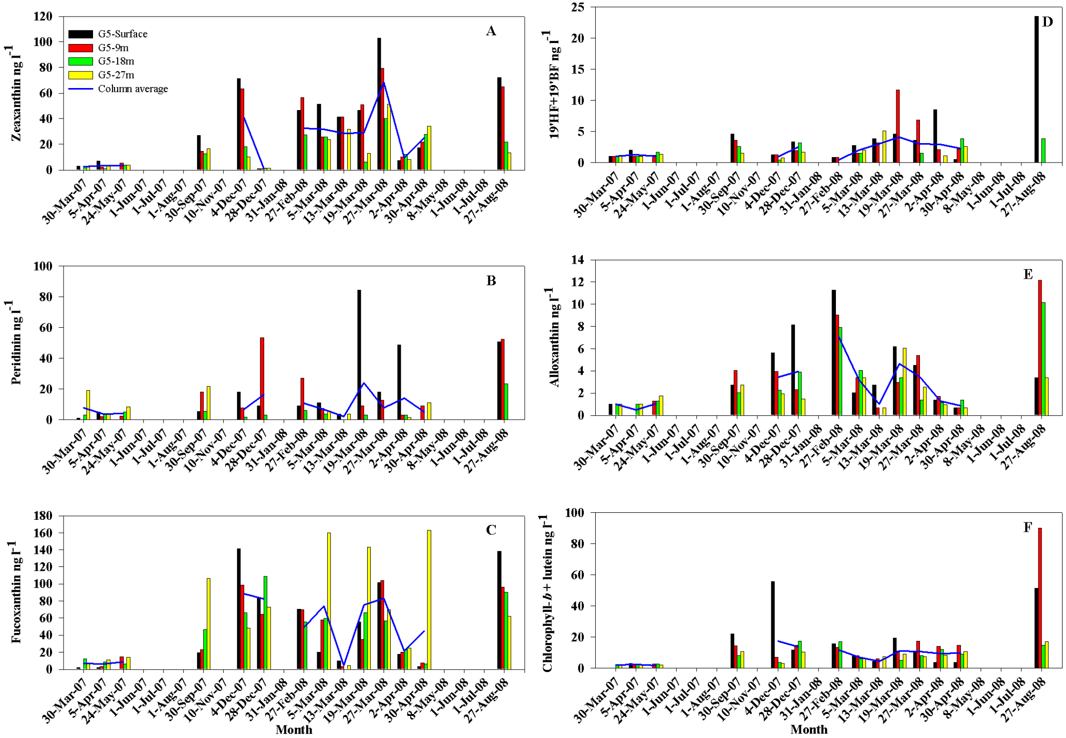

Fig. 4. Intra-annual variations of Zeaxanthin **(A)**, Peridinin **(B)**, Fucoxanthin **(C)**, 19′-hexanoyloxyfucoxanthin (19′HF), 19′-butanoyloxyfucoxanthin (19′BF) **(D)**, Alloxanthin **(E)**, Chlorophyll-*b* + lutein **(F)** at the CaTS site from March 2007 to September 2008. The three seasons (pre-monsoon, SW monsoon and post-monsoon) are marked in the figure. The bold blue line represents column-averaged values (0 m, 9 m, 18 m and 27 m) for each parameter.

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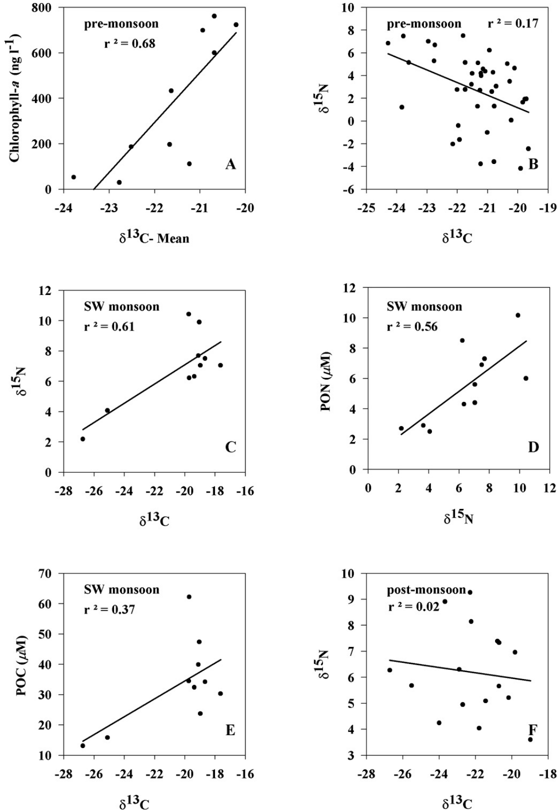

Fig. 5. (A) Correlation between mean δ^{13}C and mean total chlorophyll-*a* during pre-monsoon; **(B)** Correlation between δ^{13}C and δ^{15}N during pre-monsoon for all data points; **(C)** Correlation between δ^{13}C and δ^{15}N during SW monsoon for all data points; and **(D)** Correlation between δ^{15}N and PON during SW monsoon for all data points. **(E)** Correlation between δ^{13}C and POC during SW monsoon for all data points. **(F)** Correlation between δ^{13}C and δ^{15}N during post-monsoon for all data points.