Research Article

Seasonal variation in optically active substances at a coastal site along western Bay of Bengal

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Abstract
Optically active substances (OAS) such as chlorophyll-*a* (chl-*a*), chromophoric dissolved organic matter (CDOM) and total suspended matter (TSM) play significant role in health assessment of aquatic ecosystem. Temporal variability in OAS plays important role in modulating coastal water ecology. This demand for continuous monitoring of OAS in coastal waters. The present study highlights on temporal variability of OAS off Gopalpur, a coastal site along the north-western Bay of Bengal. The OAS were found to be having strong seasonal influence apart from large variability in concentration. Chl-*a* concentration showed fourfold variability (0.03–12.29 mg m^{-3}) with seasonal trend of pre-monsoon > post-monsoon > monsoon. Absorption due to CDOM at 440 nm ($a_{CDOM}440$) varied between 0.02 and 4.48 m^{-1} following seasonal trend of pre-monsoon > monsoon > post-monsoon. TSM concentration was ranged within 0.1–28.21 mg l^{-1} showing maximum during monsoon and minimum during post-monsoon season. The higher concentration of chl-*a* and $a_{CDOM}440$, during pre-monsoon season, was predominantly due to ecosystem disrupting red tide event of *Noctiluca* bloom during pre-monsoon season of 2014. The high load of TSM during monsoon was due to increased river influx attributed to upstream precipitation. There was no significant relation observed among the OAS indicating that multiple sources of OAS in optically complex waters of the north-western Bay of Bengal. The study provides understanding on long-term variations in OAS which is essential for development or tuning of bio-optical algorithms for accurate remote estimation of geophysical products.

Keywords Chlorophyll-*a* · Total suspended matter · $a_{CDOM}440$ · South-west monsoon · Bay of Bengal

1 Introduction

The Optically Active Substances (OAS) in the ocean water column are principally chlorophyll-*a* (chl-*a*), Coloured Dissolved Organic Matter (CDOM), and Total Suspended Matter (TSM) [24]. The differential variability in concentrations of OAS in the water column significantly determines the accuracy of ocean colour remote sensing especially in optically complex case-2 waters [9]. Therefore, region specific understanding on long-term variation of OAS is mandatory for development or tuning of well performing bio-optical algorithms for accurate remote estimation of geophysical products. In addition, the time-series observation of OAS discerns ambient water quality and ecosystem status of food chain.

In general, phytoplankton are responsible for ~ 50% of global primary production, therefore play a key role in global biogeochemical cycle. Chl-*a* is the dominant light harvesting pigment in phytoplankton and widely considered as proxy of phytoplankton biomass. Hence, concentration of chl-*a* indicates the ecosystem health. In general, phytoplankton growth is controlled by numerous factors

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viz. availability of nutrients, light, salinity, temperature and physical conditions [4]. Sometimes, phytoplankton growth occurs with abrupt increase in cell density and results massive blooms. Many regions of World Ocean are experiencing recurring episodes of mono-specific phytoplankton blooms. In general ecosystem monitoring, accounting the phytoplankton bloom is most important due to their adverse effects on water quality [11].

CDOM is the fraction of dissolved organic matter that absorbs light in the blue region of the electromagnetic spectrum [32, 36]. CDOM usually composed of humic substances, fulvic acids and other polymeric organic matter [21]. Fresh water influx from rivers and terrestrial run-off enriched with organic matters serves as important sources of CDOM to coastal waters. However, phytoplankton debris also contributes significantly to the CDOM pool in coastal and estuarine waters [16, 29]. In general, absorption of blue light by CDOM overlaps the phytoplankton absorption peak near 440 nm, resulting in a competition between CDOM and phytoplankton for light in this region of the visible spectrum [39]. Thus, introduces error while retrieving phytoplankton biomass (i.e. chl-*a*) through ocean colour remote sensing [12, 23]. A number of physico-chemical-biological processes for example, dilution of terrestrially-derived CDOM, photochemical bleaching, bacterial degradation and autochthonous production of CDOM by plankton influence the optical properties and distribution of CDOM in coastal waters [21].

TSM mainly represents the inorganic suspended material in the water column and regarded as one of the important OAS due to major role in light attenuation. In general, TSM concentration determines water clarity [35]. The presence of large concentrations of TSM in water affects the penetration of light into the water column, causes decrease in productivity of aquatic vegetations, which subsequently alter the health and quality of the water body. In context of ocean colour remote sensing, higher concentration of TSM in the ambient medium results poor performance of atmospheric correction schemes [28].

In context of OAS studies, coastal waters off Gopalpur in the north-western Bay of Bengal owes pivotal importance due to riverine influence, terrigenous runoff, recurring phytoplankton blooms etc. [5]. Although many of studies have been carried out to understand the variability of chl-*a*, TSM and nutrients in this region, no comprehensive monitoring study carried out on the OAS including CDOM [1–7]. The present study is focused on understanding the temporal variability of OAS off Goplapur, a coastal site along the north-western Bay of Bengal.

2 Materials and methods

2.1 Study site

The coastal waters off Gopalpur is an important eco-sensitive region of the north-western Bay of Bengal (Fig. 1). This region was identified for long-term time-series measurement of bio-optical and physico-chemical parameters under SATellite Coastal and Oceanographic REsearch (SATCORE) programme coordinated by Indian National Centre for Ocean Information Services (INCOIS) at Hyderabad. The region is internationally recognized for hosting annual episodes of arribada of migratory olive ridley sea turtles. Coastal water quality exhibits immense significance in favoring the periodic stay of sea turtles, re-occurrence of phytoplankton bloom and swarming of jelly fish [5]. The study area is under the significant influence of Rushikulya estuary through fresh water influx. In addition to riverine influx, coastal upwelling and anthropogenic discharge also affects biogeochemistry of the study area [27]. Annual precipitation magnitude is governed by tropical south-west monsoon which brings adequate rainfall during July–October. The circulation pattern of the study area is governed by surface current driven by monsoon winds, cyclonic circulation, and river discharge [40]. Differential distribution and variability of hydro-biological parameters in coastal waters off Gopalpur deciphered two local water types on either side of 30 m isobath. The effect of estuarine and terrigenous influx reaching up to 30 m bathymetry is the important factor responsible for formation of contrasting hydro-biological local water types [3].

2.2 Sampling and analytical methodology

In situ seawater samples were collected onboard a fishing trawler from coastal waters of Gopalpur, during several scientific surveys (84), between October 2010 and March 2017. At each station, seawater samples were collected using a Niskin sampler for estimation of chl-*a*, TSM and CDOM. The group of months March-June, July–October and November-February represent seasons as pre-monsoon, monsoon and post-monsoon, respectively.

Chl-*a* was estimated following Strickland and Parsons [38]. A known volume of water samples were vacuum filtered through 47 mm Glass Fibre Filters (GF/F). The matter retained on the filter was flooded with 90% acetone and kept overnight in dark for pigment extraction. Subsequently, the samples were centrifuged and optical densities of the supernatant were measured (at 630 nm, 645 nm and 665 nm) using a UV–visible spectrophotometer (Jasco™ double beam V-650).

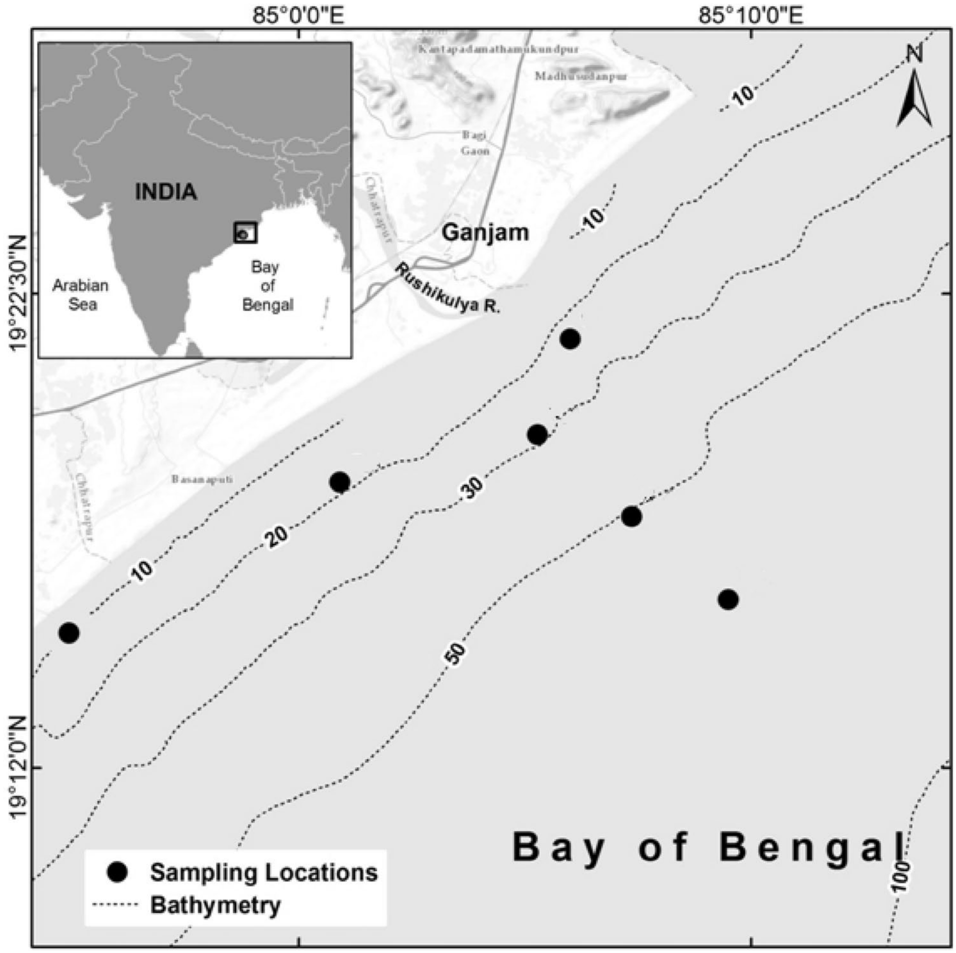

Fig. 1 Map showing study area off Gopalpur, western Bay of Bengal

TSM concentration was determined gravimetrically by filtering a known volume of water sample through 0.45 µm pre-weighed membrane filter paper. Subsequent to filtration, the filter paper was re-weighed using well calibrated electronic balance to estimate TSM concentration [38].

$a_{CDOM}(\lambda)$ was measured spectrophotometrically following Kowalczuk and Kaczmarek [22]. Seawater samples were filtered through 0.2 µm cellulose membrane filters and transferred to borosilicate glass vials and kept under low temperature until analysis. Absorbance of the filtered water samples was measured using spectrophotometer (Jasco™ double beam V-650), over the spectral range 400–700 nm at 1 nm resolution. The spectral absorption coefficient was calculated by following Eq. 1 [22].

$$a_{CDOM}(\lambda) = a_{CDOM}(440)\exp\left[-s(-440)\right]\left(m^{-1}\right) \tag{1}$$

The spectral slope, S_{CDOM}, was computed using an exponential fit from 400 to 700 nm. The absorption coefficients were also corrected for backscattering of small particles and colloids, which pass through filters by adopting following Eq. 2 [19].

$$a_{CDOM\_}corr(\lambda) = a_{CDOM}(\lambda) - a_{CDOM}(700) * (\lambda/700)\left(m^{-1}\right) \tag{2}$$

3 Results and discussion

The important aquatic OAS (chl-*a*, TSM, $a_{CDOM}440$) were observed with different ranges of variability. Histograms overlaid with trend line of normal Gaussian distribution depicted the variability in magnitude and trend of each parameter (Fig. 2). The magnitude of chl-*a* varied within 0.03–12.29 mg m^{-3} during the study period. With respect to normal, chl-*a* distribution was deviated to 60%. The chl-*a* was found to be largely varied between 0.03 and 6.45 mg m^{-3}. A patchy distribution of chl-*a* with high values were observed within 9–13 mg m^{-3}. The maximum frequency in distribution of chl-*a* (41% sample) was observed between 1 and 1.94 mg m^{-3} (Fig. 2a).

The magnitude of TSM was ranged between 0.1 and 28.21 mg l^{-1}. TSM values deviated to 34% with respect to normal trend. The TSM values were largely distributed over the range of 0.10–19.40 mg l^{-1}. Two patches of high TSM concentration were also observed at 23.70 mg l^{-1} and 28.21 mg l^{-1} during monsoon months September and August, respectively attributed to precipitation induced river/terrigenous discharge. The maximum frequencies in

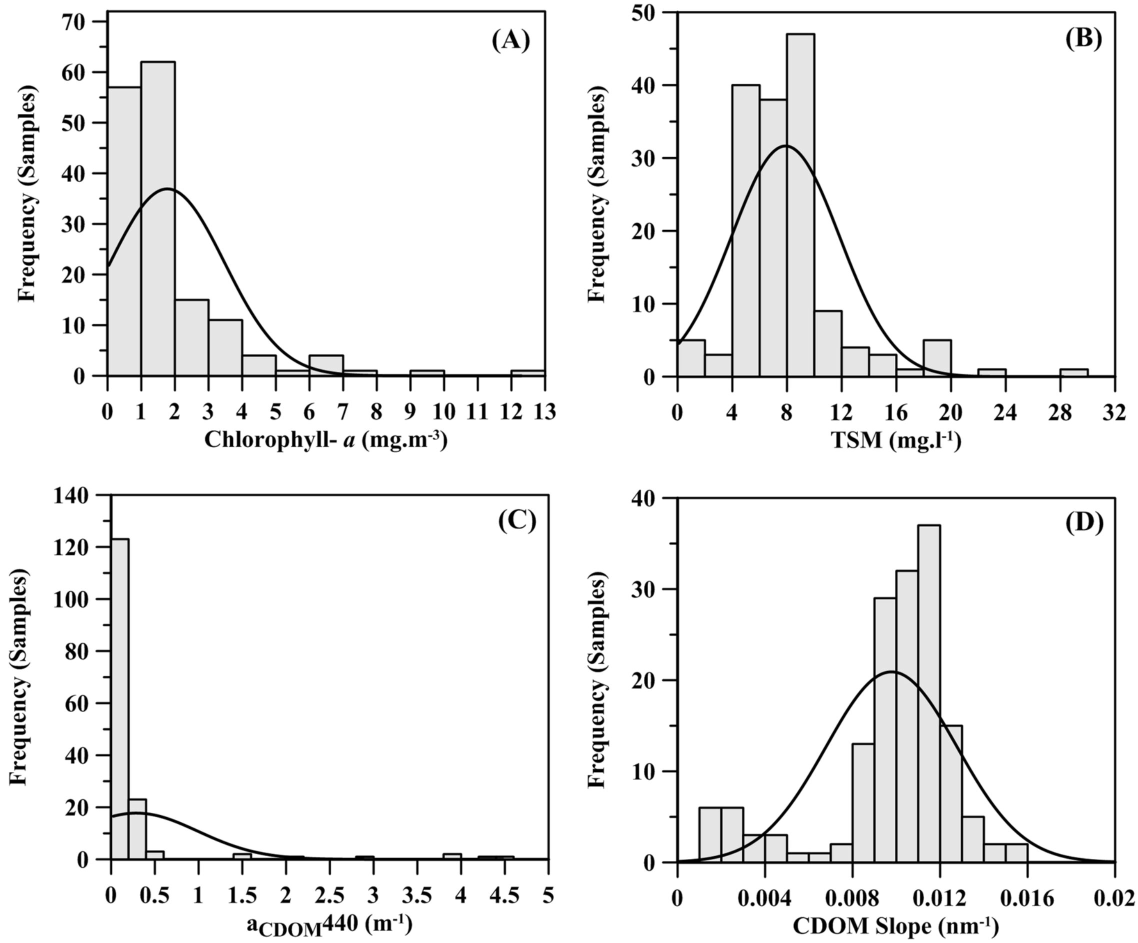

Fig. 2 Frequency distribution of (**a**) chlorophyll-*a*, (**b**) TSM, (**c**) $a_{CDOM}440$, and (**d**) slope of CDOM. The solid black line represents normal distribution of each parameter

distribution of TSM were observed within 4.10–5.90 mg l^{-1} (25.5% sample), 6.10–7.84 mg l^{-1} (24.2% sample) and 8.03–9.90 mg l^{-1} (29.93% sample) (Fig. 2b).

Several studies have been performed in the study area that recorded similar concentration of chl-*a* and TSM in corroboration with the present study. The concentration of chl-*a* was observed within magnitudes reported during earlier observations (0.12–10.05 mg m^{-3}) in the study region [3]. Most of the times, sporadic higher values of chl-*a* and TSM was observed in association with phytoplankton blooms [5, 27, 34].

The magnitude of $a_{CDOM}440$ varied between 0.02–4.48 m^{-1}. The maximum frequencies of $a_{CDOM}440$ largely varied between 0 and 0.44 m^{-1} (94.9% of samples) (Fig. 2c) ~ 100% deviation was observed in the distribution of $a_{CDOM}440$ with respect to normal Gaussian distribution. A patchy distribution of $a_{CDOM}440$ also depicted from the frequency distribution with high values within 3.5–4.48 m^{-1} (Fig. 2c). Higher magnitude of $a_{CDOM}440$ have been also reported from Swan River Estuary (3.50 m^{-1}), Tamar Estuary (3.63 m^{-1}), Mahakam Delta (5.25 m^{-1}), Chesapeake Bay-Delaware Bay (2.0–5.0 m^{-1}) and Mississippi Sound/Mobile Bay (3.13–4.27 m^{-1}) [8, 15, 20, 25]. A thorough perusal of available literature confirmed no previous study on $a_{CDOM}440$ in the study area in order to compare the range of variability. The present study is the first report of $a_{CDOM}440$ and slope parameter in the study area. However, Mishra et al. [26] observed absolute concentration of CDOM as 51.18 µg l^{-1} in the study area. Due to paucity of earlier observations, studies carried out on $a_{CDOM}440$ in nearby locations of the western Bay of Bengal were compared with the present study. Coastal waters of Vishakhapatnam, on the southern side of the study area was observed with comparatively lower range of $a_{CDOM}440$ (0.120–0.252 m^{-1}) [30]. $a_{CDOM}440$ values ranging between 0.1002 and 0.6631 m^{-1} have been reported in coastal waters off West Bengal, north of present study area [13]. The comparative higher and lower values of $a_{CDOM}440$ in view of the present study could be attributed to the degree of estuarine influence and terrigenous flux received by individual areas [14]. The magnitude of spectral slope of $a_{CDOM}440$ varied within 0.001–0.015 nm^{-1}. The peak frequency of spectral slope of $a_{CDOM}440$ varied within 0.008–0.01 (26.75% samples) and 0.01–0.012 (43.94% samples) (Fig. 2d). The spectral slope of $a_{CDOM}440$ deviated to 21% with respect to normal.

The frequency distribution provided the information on overall variability in OAS over the study period. However, the study area has been reported as a seasonally dynamic ecosystem [3, 5]. In context of seasonal variability in chl-*a* concentration, higher range (0.35–12.29 mg m^{-3}) was registered during pre-monsoon months while lower (0.46–3.89 mg m^{-3}) during monsoon. The monthly variability of all parameters was assessed for study period which discerned large variability (Fig. 3). In this study, monthly average concentration of chl-*a* was observed between 0.83 (June) and 3.79 mg m^{-3} (April). As similar to the highest average concentration, the highest magnitude of chl-*a* was also observed during April (2014). Baliarsingh et al. [5] have reported a dense mono-specific proliferation of red tide forming *Noctiluca scintillans* during April of 2014 with chl-*a* concentration reaching up to 12.3 mg m^{-3}. In general, the study area experiences recurring algal blooms during pre-monsoon months. A study on algal bloom associated with diatom *Asterionellopsis glacialis* in coastal water of Gopalpur was observed with chl-*a* values reaching up to 238 mg m^{-3} [34].

The occurrence of bloom in the Bay of Bengal is influenced by several physico-chemical and biological processes [17, 31]. In general, phytoplankton blooms were recorded during pre-monsoon season in the study region [5, 34]. Local upwelling induced nutrient recharge of water column triggers recurring algal bloom in the study area [18]. In addition, stable water temperature and muggy weather without rain are considered as conducive conditions for algal bloom, especially proliferation of *N. scintillans* in the study area [27]. The seasonal trend of chl-*a* was observed as pre-monsoon > post-monsoon > monsoon over the study period. The highest concentration of chl-*a* (12.29 mg m^{-3}) was observed during pre-monsoon attributed to intense bloom of *N. scintillans*. The monsoon season was observed with lowest magnitude of chl-*a* (3.89 mg m^{-3}) (Fig. 3a). Freshwater influx due to monsoonal precipitation, higher river discharge and cloud cover retards phytoplankton growth during monsoon period [3]. After withdrawal of south-west monsoon, chl-*a* concentration was observed higher (4.78 mg m^{-3}) in comparison to monsoon. Increase in water column transparency, reduction in cloud cover and availability of nutrients introduced during previous season (monsoon) could have fuelled phytoplankton growth during post-monsoon.

The other important OAS, TSM concentration (monthly average) varied from 5.59 to 12.23 mg l^{-1} during the study period (Fig. 3b). The seasonal rank order of TSM concentration was observed as monsoon > pre-monsoon > post-monsoon. Influx of inorganic matter to the coastal water attributed to precipitation induced river and terrigenous runoff during south-west monsoon resulted in higher concentration of TSM (28.21 mg l^{-1}). Despite lower river and terrigenous run off during pre-monsoon season, higher values of TSM during pre-monsoon (maximum 19.4 mg l^{-1}) signified local perturbations. As like chl-*a*, increased values of TSM was also observed during pre-monsoon (April 2014) in association with the red tide [5]. TSM concentration varied within 3.2–15.7 mg l^{-1} during post-monsoon period. Decrease in land runoff and stabilization of water column during post-monsoon could have resulted comparative decline in TSM.

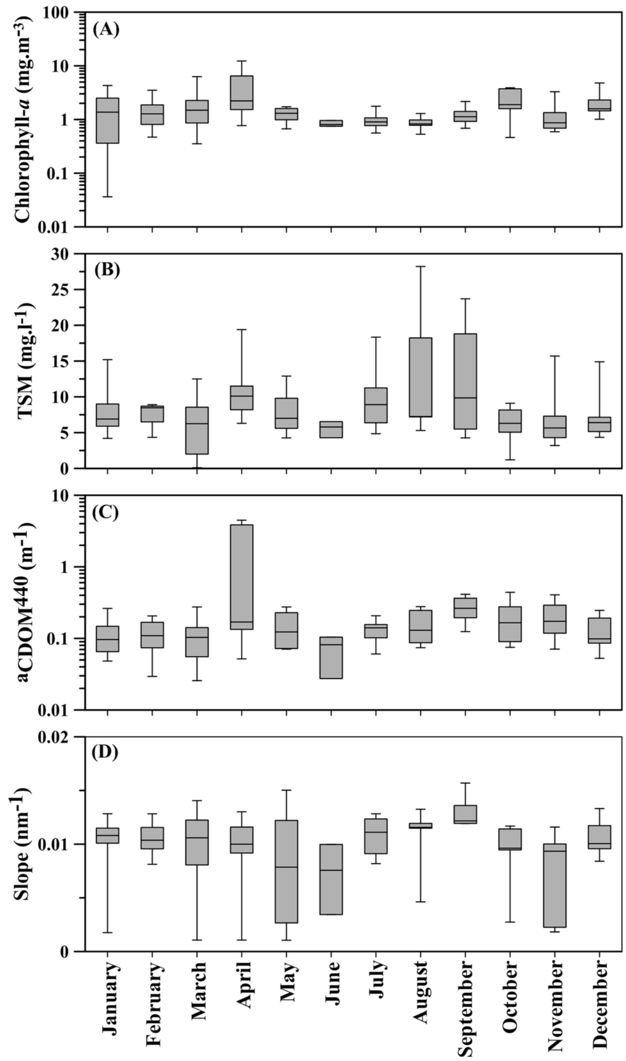

Fig. 3 Monthly Box–Whisker diagram of (**a**) chlorophyll-*a*, (**b**) TSM, (**c**) $a_{CDOM}440$, and (**d**) slope of CDOM. The central bar represents the median. The box represents interval between the 25 and 75% percentiles. The whisker indicates the range

The distribution of a_{CDOM}440 was more dynamic at temporal scale in comparison to other OAS viz. chl-*a* and TSM (Fig. 3c). At temporal scale, monthly average magnitude of a_{CDOM}440 varied between 0.07 and 1.44 m^{-1}. The highest value (0.02–4.48 m^{-1}) was encountered during pre-monsoon (April), whereas lowest magnitude (0.02–0.4 m^{-1}) during post-monsoon (November). The higher absorption of CDOM during March and April substantiated the higher values of a_{CDOM}440 in the pre-monsoon period. Seasonal variability of a_{CDOM}440 followed the rank order of pre-monsoon > monsoon > post-monsoon. Higher magnitude of a_{CDOM}440 during pre-monsoon season could be sourced from the co-prevailing higher concentration of phytoplankton biomass (i.e. chl-*a*) [14, 33]. In general, phytoplankton degradation and bacterial metabolism contribute significantly to CDOM magnitude in the ambient medium [10]. The higher value of a_{CDOM}440 was observed during the pre-monsoon season of 2014 in association with red *Noctiluca scintllans* bloom. The degraded matter of the bloom could have resulted with increased values of a_{CDOM}440.

The magnitude of a_{CDOM}440 was ranged within 0.06–0.44 m^{-1} during monsoon period. In contrast to the present observation, the seasonal trend of a_{CDOM}440 was observed highest in monsoon season and least in other non-monsoon seasons in coastal waters off West Bengal, north of present study area [13, 14]. The difference in a_{CDOM}440 variation pattern between these two locations could be attributed to the effect of pre-monsoon phytoplankton bloom. The monthly mean of spectral slope of CDOM varied between 0.007 and 0.012 nm^{-1} (Fig. 3d). Lower range of variation in spectral slope of CDOM was observed during different monsoon months while higher during pre-monsoon months. In general, slope parameter in context of CDOM deciphers the source. The higher and lower ranges of variation in slope indicate autoconthous and alloconthous origin of CDOM, respectively [37]. Das et al. [13] have reported spectral slope of CDOM ranged within 0.007–0.0229 nm^{-1} in coastal water of West Bengal (north of present study area). During a study in coastal water off Visakhapatanam (south of present study area), Pandi et al. [30] have reported spectral slope of CDOM from 0.009 to 0.020 nm^{-1}. The range of spectral slope of CDOM observed during the present study (0.001–0.015 nm^{-1}) is concomitant to the studies mentioned above.

The magnitude of chl-*a*, TSM and a_{CDOM}440 collectively determines the inherent optical properties of ambient medium. In general, CDOM is a byproduct of phytoplankton and/or from terrestrial input in ocean. Hence, CDOM absorption may be related to phytoplankton biomass [33]. Higher magnitude of CDOM was also earlier reported in vicinity of the study area with no significant relation with chl-*a* [26]. Therefore, river influx/terrestrial run off could have played major role in input of CDOM to coastal waters [26]. No significant relation in variability of a_{CDOM}440 with chl-*a* as well as TSM was also observed in coastal waters off West Bengal, north of the study area attributed to river influx [13]. In addition, no relation in trend of a_{CDOM}440 and slope indicated complex nature of CDOM dynamics in the study area resulting difficulty in source identification. In general, the non-significant relation observed among the OAS indicated multiple sources of OAS in optically complex waters of north-western Bay of Bengal.

4 Conclusion

The present study reports a comprehensive long-term analysis of OAS (CDOM, TSM, chlorophyll-*a*) in an ecologically dynamic coastal site along east coast of India (western Bay of Bengal). The outcome of the study is summarized as (1) large range of variability in OAS, (2) seasonality in OAS distribution, (3) riverine/terrigenous influence along with monsoon forcing on OAS dynamics, (4) pre-monsoon preponderance of phytoplankton leading to bloom, (5) upsurge in CDOM magnitude as a consequence of *N. scintillans* red tide. In general, the study represents the coastal waters off Gopalpur as an optically complex ecosystem suggesting development of region specific ocean colour models for satellite retrieval of OAS.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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