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Observations on physico-chemical variability of seawater along Tamil Nadu coast, India onboard CRV Sagar Purvi

K Priyanka[a], R K Sarangi[b], A Saravanakumar*[,a], G Suthagar[a] & D Poornima[a]

[a]Centre of Advanced Study in Marine Biology, Annamalai University, Parangipettai, Tamil Nadu – 608 502, India

[b]Marine Ecosystem Division, BPSG/EPSA, Space Applications Centre (ISRO) Ahmedabad – 380 015, India

*[E-mail: asarvaan@gmail.com]

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Parameters that define the environmental variables, such as, phytoplankton biomass, chl-*a*, and nutrient concentration have been studied and analyzed during July 2017. During this study, vertical distribution of physico-chemical and water quality parameters has also been analyzed. Decrease in water temperature and dissolved oxygen from the surface to deep water up to the thermocline and oxycline were observed, which would be in relation to oxygen minimum zone. At the depth of 100 m, the concentration of chl-*a* is found high as compared to the surface water. The estimation of deep chlorophyll maximum has been chosen as a major investigation in this study. Moderate and high chl-*a* concentration (0.5-2.8 mg m^{-3}) regardless of less NO_3 flux (0.01-0.6 µM) have been recorded through *in-situ* and satellite observations. The concentration of SiO_4 (5-35 µM) is likely enhanced in the vertical and surface water productivity. Principal component analysis and multiple linear regressions were carried out in order to determine the difference of the variables between the surface and deep water.

[**Keywords**: Nitrate imaging, Physico-chemical parameters, Chlorophyll-*a*, Vertical distribution of nutrients]

Introduction

The major biotic component in the oceanic biological system is phytoplankton[1]. The temporal variations in phytoplankton biomass are caused due to the complex interaction of physico-chemical and biological process[2]. The upshot of marine phytoplankton realm is the primary productivity which is highly reliant on light penetration, nutrient availability and depth of mixed layer of water column[3]. To estimate this, several examinations have been conducted on various physical and chemical parameters in the Bay of Bengal (BoB)[4,5]. In addition to this, investigation on marine productivity and ecosystem has also been carried out in BoB to assess their seasonal and spatial behavior[6,7] in which not many research has been carried out so far except few[4,5]. Despite of major focus of present research is toward the vertical distribution of nutrients along with the observations on oxycline and thermocline, including the deep chlorophyll maximum (DCM) after the summer season.

The concentration of nitrate (NO_3) plays a crucial role in the new production and high productivity zones in different seasons. Surface NO_3 dynamics is essential for marine productivity on ecological time scales. Among all the nutrients, nitrogen (N) is the most important and common element which limits the primary and secondary production in the aquatic ecosystem[10], although phosphorus (P) at times replaces N as the most limiting nutrient in certain marine habitats[11] depending upon the composition of phytoplankton communities. Hence, the estimation of NO_3 has gained significance for the BoB region so as to know the biogeochemical processes prevailing in the study area. Enrichment of marine nutrients also occurs through internal physical processes such as upwelling and mixing that re-suspend nutrients from the deeper volumes of water column by bringing nutrient-rich water to the sea surface.

The aim of the current study is to understand the peculiarities in the physico-chemical parameters of pre-monsoon season, especially the nutrients such as NO_3, ammonia (NH_3), inorganic phosphate ($_IP(PO_4{}^3)$ and silicate (SiO_4) along with chlorophyll-*a* (chl-*a*) concentration. The present investigation is an attempt to observe satellite-based sea surface temperature (SST) and chl-*a* characteristics of the coastal waters of the southwest BoB, using the Ocean Color Monitor (OCM), Moderate Resolution Imaging Spectroradiometer (MODIS) and the derived NO_3 images. The data obtained during the present study is analyzed using advanced statistical techniques such as Principle Component Analysis (PCA) and Multiple Linear

Regression (MLR), which are been widely utilized now in the analysis of nutrient data for a meaningful data reduction and interpretation[5].

Materials and Methods

In-situ sea water samples were collected from Chennai, Kalpakkam, Cuddalore, and Poompuhar. These are the major prominent coastal stations along the coast of Tamil Nadu, BoB. All the seawater samples were collected onboard the Coastal Research Vessel (CRV) Sagar Purvi from 7th to 11th July, 2017 (Fig. 1) during daytime from standard depths of surface, 10, 25, 50 and 100 m. In total, 80 samples were collected for assessing the physico-chemical and biological parameters of water, *viz*., chl-*a*, pH, Dissolved Oxygen (DO), Salinity, Water Temperature (WT), NO_3, NO_2, NH_3, SiO_4 and $_IP(PO_4^3)$.

WT and salinity were measured utilizing digital multisensor of ±0.01 °C accuracy (Merck Millipore-Multi 3420) and DO was estimated by the Winkler's method[10]. Dissolved nutrients such as NO_3, NO_2, NH_3, ($_IP(PO_4^3)$ and SiO_4 were estimated following the standard methods described by Strickland & Parsons[10]. For Chl-*a* estimation, sea water was filtered using a 47-mm diameter GF/F filter paper and extricated using 90 % acetone and was determined with a Shimadzu UV 2450 spectrophotometer (Shimadzu, Inc., Tokyo).

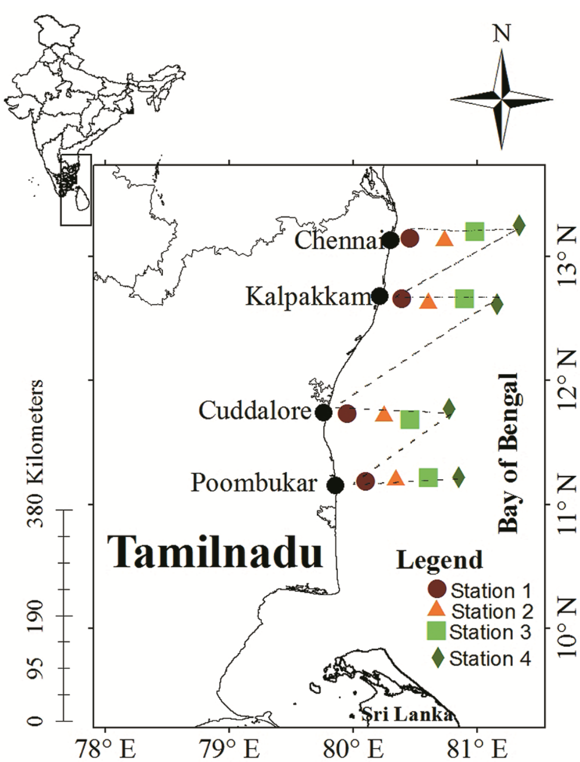

Fig. 1 — Sampling position during CRV Sagar Purvi 2017

SST and chl-*a* are the most important parameters in oceanography, marine meteorology, and primary productivity. Hence, cloud-free satellite images were downloaded from the OCM level 2 processed chl-*a* data obtained from the Space Application Centre (SAC), and the National Aeronautics and Space Administration (NASA) MODIS Aqua level 3 processing data acquired from NASA's MODIS website for SST. The satellite images were color coded and gridded using ERDAS Imagine ver. 9.1 and Envi ver. 4.7 software for interpretation.

Statistical analysis

Principal Component Analysis (PCA) and Multiple Linear Regression (MLR) analyses were used to study the relationships between the different marine environmental variables and chl-*a*. PCA was utilized to analyze the marine environmental parameters for tracing the fundamental pattern through all the variables and reduced the number of variables to obtain accuracy. The MLR analysis has been used to calculate the value of a dependent variable, with a set of predicted variables which could facilitate to decide the extent and know the variables contribution too[11]. These analyses were done using SPSS ver. 11.5 statistical software. Physico-chemical parameters were indicated using the Sigma plot version 12.3.

Results and Discussion

Hydrobiological parameters of the seawater are considered as the main significant features, capable of influencing the growth, diversity, and abundance of phytoplankton in the oceanic environment, and they show broad spatial and temporal variations. However, the current study pertains to the distribution pattern of nutrients (horizontal and vertical) and their rate of utilization during the cruise period along the Chennai, Kalpakkam, Cuddalore, and Poompuhar.

Water temperature (WT)

In physico-chemical parameters, water temperature is most important hydrographical parameter, which affects almost every chemical and biological interactions[12]. During the present study, water temperature was observed to decrease rapidly from surface to deeper waters (29.9 to 21.1 °C), registering the minimum at 100 m depth (Kalpakkam) and maximum at the surface (Chennai). The gradual decrease in the WT was observed at the depth of 100 m in all the four stations (Chennai, Kalpakkam, Cuddalore, and Poompuhar) (Fig. 2a-d) indicating the

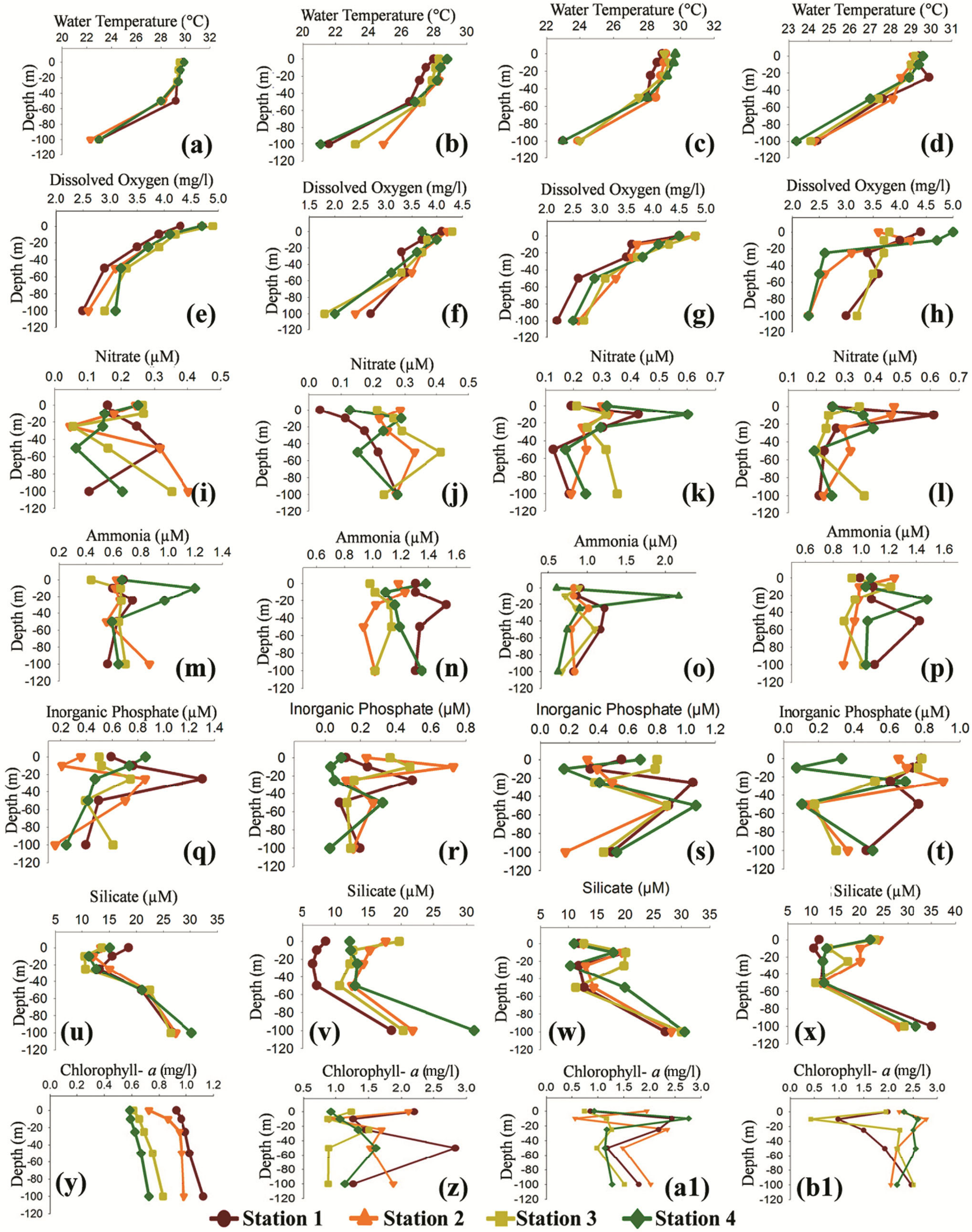

Fig. 2 — Vertical profile of water temperature, dissolved oxygen, nitrate, ammonia, inorganic phosphate, silicate and Chl-*a* at: a,e,i,m,q,u,y) Chennai; b,f,j,n,r,v,z) Kalpakkam; c,g,k,o,s,w,a1) Cuddalore; and d,h,l,p,t,x,b2) Poompuhar

strongest stratification in water temperature at the depth of 50 and 100 m (approximately in range of 4.2 °C). Wijesekera *et al.*[13] reported the fluctuations in temperature of vertical water column as large as ±3.5 °C, which were limited to the major thermocline layer (50 – 150 m).

Dissolved Oxygen (DO)

DO concentration varied between 1.8 and 5.0 mg l^{-1}. The maximum value was observed in the surface waters of Poompuhar (station 1) and lower value at 100 m depth at Kalpakkam (station 4). Higher DO levels was observed at the surface waters and was decreased rapidly with depth (Figs. 2e – h). Generally, DO distribution is controlled by physical processes, such as, atmospheric interactivity, upwelling, freshwater influx, and biological processes like photosynthesis and respiration.

Water shows highly stratified and the weaker wind breaking this stratification prohibits circulation between water masses leading to lower oxygen into the deepwater column. As the alongshore winds and upwelling is weaker in the BoB compared to the Arabian Sea, west coast along with high freshwater input in the Bay, results in stratification and thinner surface mixed layer. Hence, the result showed horizontal advection of highly oxygenated water due to oxygen depleted subsurface water is pumped into the surface water by upwelling during the pre-monsoon in all the four stations of Chennai, Kalpakkam, Cuddalore, and Poompuhar, which is formed at the surface through air-sea interaction. Furthermore, these hydrographic changes, leads to low primary production in sea surface, reduction of nutrient entrainment in the euphotic zone and remineralization at depth. This is also one more reason which caused Oxygen Minimum Zone (OMZ) to remain reduced in BoB[14,15].

Nutrients

NO_3 level was minimal (0.011 µM) at 50 m depth in Cuddalore (station 3) and was maximum (0.612 µM) at the subsurface waters (10 m) in Poompuhar (Station 1). In general, NO_3 showed lower values at the surface layers of all the stations (Figs. 2i – l), which were increased gradually in the subsurface (from surface to 25 m), indicating that there could be coastal upwelling in Bay of Bengal[16]. At 100 m depth, the NO_3 concentration started to decrease and this may be due to the increased bacterial respiration rates in the OMZ[17].

The level of ammonia varied between 0.437 µM Chennai, (surface water station 3) and 2.11 µM (Cuddalore, at 10 m station 4). The average ammonia level observed was 1 µM (Figs. 2m – p). It has been reported that the highest concentrations of NH_3 are found where the bacterial denitrification processes utilize NO_2 and thus produce N and NH_3[ref. 18]. The occurrence of nitrification process has been clearly indicated in the subsurface water (20 m depth) at station 4. Fluctuation in nutrients and primary productivity controls the dynamics of phytoplankton group, for example, it was observed that NH_3 could be utilized as the limiting nutrient when compared to NO_2 in controlling the development of the phytoplankton[18].

$_IP(PO_4^3)$ content varied between 0.026 µM at 100 m depth of Kalpakkam (Station 4) and 1.306 µM at 50 m depth of Chennai (Station 1). Figures 2(q – t) shows that it is enormously present at Chennai, Kalpakkam, Cuddalore, and Poompuhar near coastal regions (stations 1 & 2) when compared to the offshore (stations 3 & 4). The major factor that enhances the phosphate (PO_4^3) concentration is the swapping of phosphorous (P) between the marine water and sediments through interstitial marine water as well as through the regenerative property of the sediments[19].

SiO_4 level showed the variation from a minimum of 5.078 µM at the depth of 25 m in the inshore of Kalpakkam (Station 1) to a maximum of 35.124 µM at 100 m depth of Poompuhar (Station 1) at the depth of 100 m. Figures 2(u & v) clearly depicts that the SiO_4 level increased from the surface toward the depth in Chennai and Kalpakkam upto 100 m, but in Cuddalore and Poompuhar (Figs. 2w & x), it showed the expansion from the surface toward the depth of 50 m. SiO_4 tends to accumulate in deep water due to the presence of detrital material of diatoms along with the sources from sediments[20]. However, the cycle of SiO_4 has obtained a significant attention in relation to its role in marine primary production in the last few decades[21]. Only diatom, the greatest diverse group of phytoplankton, shows the vital role in organic matter enrichment to the deep sea, requiring silicon, N and P[ref. 22].

Chl-*a* concentration varied from a minimum of 0.563 µg l^{-1} at 10 m depth in Cuddalore (station 2) to a maximum of 2.828 µg l^{-1} at a depth of 50 m in Kalpakkam (station 1). Chl-*a*, which is the most important photosynthetic pigment in the oceanic phytoplankton, is employed as a specific biomass indicator of phytoplankton or else productivity in the ocean[23]. Figures 2(y & z) shows the rapid increase of chl-*a* from the surface to the depth (100 m) in Chennai and Kalpakkam. Other stations in Cuddalore and Poompuhar displayed a slight fluctuation at the depth of 50 m. When compared to the sea surface, chl-*a* is plentiful at the depth of 100 m. The vertical stratification of the water column in Figures 2(y –b1) is slightly weak in shallow water areas, above the nutrient-rich deep sea water, specifying their well-known ability to biological activities adopted to low nutrient conditions[24,25]. Unless other vertical processes take place such as mixed layer depth, upwelling, Ekman pumping and thermocline[26,27]; the phytoplankton shows the uptake of nutrients in the euphotic zone and thus enhance the Deep Chlorophyll Maximum (DCM)[28]. Such DCMs are the rendering features in the major parts of tropical and subtropical oceans[29].

Vertical distribution of the physical parameters, showed a rapid decrease of temperature and DO from the surface to depth (100 m). The presence of a higher DO level near the sea surface water is due to the presence of phytoplankton that release oxygen during photosynthesis[30,31]. Intensity of the sunlight in the ocean decreases with the increasing depth and hence the decrease in photosynthetic activities of phytoplankton. Further, a reciprocal relationship is observed between the phytoplankton and light intensity[32,5]. Occasionally, the increased light intensity might increase the SST, which tends to deplete the phytoplankton communities. This is endorsed from the negative correlation observed between phytoplankton density and WT.

Development of phytoplankton is driven by nutrient availability, temperature, and irradiance. All the three variables change suddenly in the DCM layer and are almost synchronous and opposite to the temperature and light conditions which become less favourable with depth (darker and colder water) although nutrient concentrations increase in the depths below 50 m. At high turbulent diffusivity, DCM tracks the seasonal changes in light conditions. Once turbulent diffusivity is depleted, DCM exhibits a phenomenon called *phase locking*, in that oscillations were squeezed within the seasonal cycle[28]. Stratification caused by the discharge of freshwater input is thought to limit the upwelling of nutrients in the depths. However, stratification in the southern Bay of Bengal was weaker than north[33,34] and the vertical distribution of nutrients in the present study showed that this is not strong enough to prevent the upwelling of nutrients.

NO_2 has an eminent role in the primary and new production zones of different seasons in the BoB. Upwelling waters have also enriched the concentrations of nutrients since this originate near the ocean floor water. Numerous species of phytoplankton have different chlorophyll-*a* concentrations and they appear in various colors, and are sensitive to satellite detection. There have been few seasonal NO_3 algorithms (parabolic fit) developed recently[35,36] using *in-situ* NO_3 data. SST and chl-*a* datasets of the region have been utilized for generating the NO_2 algorithm.

The OCM derived chl-*a* image (Fig. 3a) showed high chl-*a* concentration (0.5 – 2.0 mg m^{-3}) near the

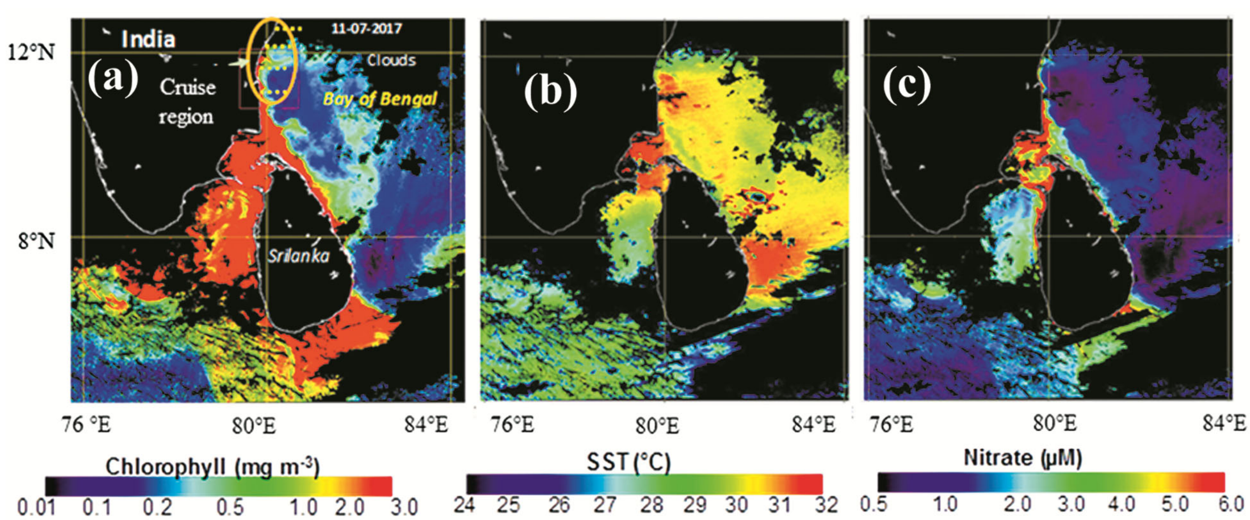

Fig. 3 — a) Oceansat-2 OCM derived chlorophyll-*a*, b) Modis-Aqua derived SST and c) modeled nitrate images

coastal water, as observed in the cruise region between Poompuhar and Chennai. The offshore water locations off the northern Tamil Nadu coast showed lower chl-*a* concentration in the range of 0.2-0.5 mg m^{-3}. In addition, taking account of the time of collection the *in-situ* data differed at different stations during the daytime as compared to that of the satellite overpass. However, it is challenging to get a pretty correct correlation in the validation of *in-situ* data with satellite datasets due to excessive cloud cover over the BoB. SST image (Fig. 3b) shows the variation of temperature in two distinct ranges and categories. In the cruise experimentation region, comprising of northern Tamil Nadu coastal and offshore water and off Sri Lankan east coast waters, the SST observed is relatively high, almost in the range of 28-32 °C. The southern region, below 7° latitude, experienced low SST in the range of 24 – 28 °C. The low SST in the study area and in the cruise region indicate that there is no pulling off the northern Tamil Nadu coast during this month and season, unlike what happens in the west coast off Kerala with effect of the Southwest monsoon. Therefore, a low nutrient flux and lesser chl-*a* concentration are observed in the chl-*a* and NO_3 images (Fig. 3c). There is no observation of river and estuarine fluxes in the study area. Hence, the low chl-*a* concentration in satellite images along the cruise sampled data points seems to be convincing.

Principle Component Analysis (PCA)

Surface (0 – 10 m)

PCA was computed using the standardized dataset; the components with eigen values ≥ 1 were known for smooth interpolation. The physico-chemical variables and chl-*a* were subjected to PCA using varimax rotation. In this present study at the surface, three factors of PCs were extracted, and this explained the cumulative variance of 69.67 % (Fig. 4a). PC1 explained 35.38 % of total cumulative variance related to high range of positive loadings of NO_3 (0.896) and chl-*a* (0.818); moderate positive loading of SiO_4 (0.661) and NO_2 (0.549) and strong negative loadings of DO (-0.804) and water temperature (-0.782). The temperature indicated significant inverse relation to the nutrients (NO_3, NO_2, and SiO_4), chl-*a* and DO in the surface waters. The correlation statistics reflects the high cold-nutrient rich water within the euphotic zone, which is consequently warmed through incoming solar radiation and reduced by phytoplankton utilization[37,5]. PC2 explains positive loadings of chl-*a* (0.500), NO_2 (0.577) and a strong negative loadings of salinity and NH_3. NH_3 fluctuation in the marine condition could be attributed to its oxidation and reduction ability so as to be converted into different forms of N. Thus, NO-N is consumed only when NH_3 is exhausted[5,38]. There was moderate rainfall during the sample collection at Poompuhar, leading to decreased salinity and increase in chl-*a* with NO_3. The combined effect of rainfall and alongshore wind results in the formation of new nitrate components (new production) and strong stratification due to low salinity enhance the abundance of phytoplankton. Overall, the heavy rainfall induces land runoff that reduced salinity, lowered transparency, and that an increased surface wind accompanied by precipitation events played a significant role in the observed changes in the chl-*a* concentration in the bay water. The third component explains the strong positive loading of pH (0.920).

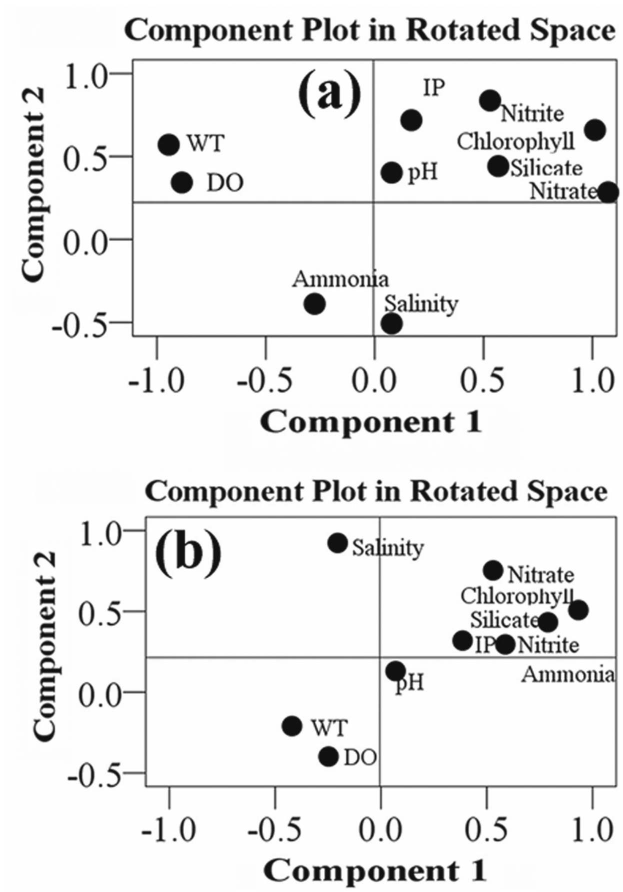

Fig. 4 — Rotated component loading plots: a) surface to 10 m depth and b) 25 to 100 m depth

Depth (25 – 100 m)

In the subsurface, the measured physico-chemical variables describe 75.77 % of cumulative variance with three components (Fig. 4b). PC1 explains only a strong positive loadings of Chl-*a* (0.893), NH_3 (0.863), NO_2 (0.845), SiO_4 (0.825), NO_3 (0.739), and $_IP(PO_4^3)$ (0.705). The nutrients such as $_IP(PO_4^3)$, NO_3, NO_2, and SiO_4 are important parameters responsible for biological primary productivity and growth with utilization of SiO_4 and NO_3. However, solar radiation attenuates with depth, resulting in delimited zone where phytoplankton photosynthesis can occur only in the euphotic zone and the absorption of sunlight causes surface water to be much warmer than the underlying deep water. In this case, phytoplankton cannot increase the biomass and hence the photosynthesis remains lower[34]. The chl-*a* maxima occurs at a depth where there is an adequate concentration of nutrients and light for photosynthesis[40]; hence, the regenerated nutrients play a vital role in deciding DCM depth in the open sea. PC2 showed negative loading of salinity, DO, and water temperature. There was a high correlation of halocline, oxycline, and thermocline. DCM is located below the surface mixed layer in halocline, oxycline and thermocline, and this cruise coincided with the deep chl-*a* maximum at depth of 25 and 50 m, respectively. Hypothetically, it is stated that subsurface water samples should experience the enriched nutrient contribution in the deeper region[41]. As observed in the present study, in deeper waters, chl-*a* is high along with nutrients such as NO_3, NO_2, inorganic phosphate, and SiO_4. Such condition creates a deeper DCM, exactly matching with the nutricline, usually corresponding to a phytoplankton or biological activity that indicates the biomass maximum. Unless other vertical processes take place, phytoplankton keep on reducing the nutrient contents in the euphotic zone and subsequently developing the DCM layer[27,28]. The third component revealed a strong positive loading of only pH (0.949).

Multiple Linear Regressions (MLRs)

A correlation matrix between hydro-biological variables and chl-*a* concentration done using MLR during all the surface and subsurface experiments yielded the following equations 1 and 2, respectively. Chl-*a* concentration is contemplating to the response variable, and the other hydrobiological variables are considered as explanatory variables.

$$Chl = -150.39 + 0.76\,(WT) + 0.67\,(DO) - 1.80\,(salinity) + 24.28\,(pH) - 2.44\,(NO_2) - 0.18\,(NO_3) + 0.46\,(NH_3) - 3.78\,(_IP(PO_4^3)) + 0.19\,(SiO_4) \quad \ldots (1)$$

Equation 1 shows that chl-*a* concentration determines the integrated positive influence with WT, DO, pH, NH_3, and SiO_4 in surface waters up to 10 m. It indicates that the above-mentioned factors are responsible for chl-*a* significantly contributed by diatom populations, which in turn resulted in the increased DO levels in the vertical water column owing to photosynthesis by phytoplankton biomass and rainfall. Higher DO present in the sea surface is due to higher solubility of oxygen in the less saline sea surface water available in pre-monsoon season[42,43]. The equation states that a negative correlation is observed between NO_2, NO_3, and $(_IP(PO_4^3)$ along with chl-*a*. The analysis includes the subsurface datasets up to 10 m depths; the effect of temperature is not largely exaggerated in the regression analysis.

$$Chl = -115.58 - 0.13\,(WT) + 0.77\,(DO) + 1.14\,(Salinity) + 9.76\,(pH) + 8.33\,(NO_2) - 0.25\,(NO_3) + 0.23\,(NH_3) + 2.83\,(_IP(PO_4^3) + 0.08\,(SiO_4) \quad \ldots (2)$$

Equation 2 states that the regression analysis shows a positive relationship of DO, pH, salinity, and nutrients like NO_2, NH_3, IP, and SiO_4 with chl-*a*. The negative correlation of NO_3 and temperature implies the inverse relationship between temperature and chl-*a* concentration due to significant phytoplankton communities in the BoB[44]. Furthermore, a negative relationship of nutrients such as NO_3 points here that the nutrients are consumed by phytoplankton[45].

The results of regression equation 1 showed that the $R^2 = 0.48$ and N = 32 with SEE = ±3.25, depict that approximately 35 % of the chl-*a* concentration is accounted by the variables at the surface for total stations among the predicted factors. Equation 2 depicts a significant correlation with $R^2 = 0.53$, N = 48 and SEE = ±2.77.

Conclusion

This study is an attempt to relate the vertical distribution of nutrients with chl-*a*, temperature and DO. It showed that WT and DO rapidly decrease from surface to depth (100 m), owing to stratification and weaker upwelling to form the Oxygen minimum zone (OMZ). In theory, that the vertical distribution of nutrients in water column described here is reproducible down to the DCM layer with low light and high nutrient patterns. The role of SiO_4 is observed to be predominant over NO_3 as the limiting nutrients in the Bay of Bengal region during the pre-monsoon season. Further investigation is necessary to be made incorporating seasonal analysis with the fine structure of vertical alignment of nutrients, chl-*a* and DO. This would assist in better understanding of the ecological traits of phytoplankton communities, DCM and OMZ.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Conceptualization: AS & RKS; Parameter analysis: GS & KP; software: KP & RKS; Formal analysis writing, original draft preparation: KP; and Review and editing: DP, AS & RKS.

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