

## Satellite and In situ observations of a phytoplankton bloom from coastal Bay of Bengal: Role in pCO<sub>2</sub> modulation

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### Abstract

A phytoplankton bloom was monitored in coastal waters of Bay of Bengal and its influence in water column properties was investigated. Significant draw down of CO<sub>2</sub> was noted within the vicinity of the bloom associated with high chlorophyll biomass. Microscopic analysis revealed diatoms as the dominant population. *Skeletonemacostatum* diatom, reached cell density of 36898 cells l<sup>-1</sup> within the bloom. The lowest surface pCO<sub>2</sub> observed was 287 μatm at the southern end of the transect covarying with surface chlorophyll of 1.090 μg l<sup>-1</sup>. At the northern end the surface pCO<sub>2</sub> went as low as 313 μatm. The pCO<sub>2</sub> levels below the mixed layer increased twice of that of surface value (~ 600 μatm). The chlorophyll values observed by Ocean Colour Monitor-2 (OCM) were modestly related with the in situ measurements. The primary productivity derived from growth rate, assimilation number and maximum surface chlorophyll was 160.6 mg C m<sup>-2</sup>day<sup>-1</sup> leading to a modest sequestration ~ of 0.08 Gg of carbon per day by the surface waters. Our observations reflect the potential role of diatom bloom on coastal carbon dynamics therefore should be carefully monitored in realm of anthropogenic changes.

**Keywords:** Phytoplankton; Algal bloom; *Skeletonemacostatum*; Productivity; carbon; Chlorophyll;

## 1. Introduction

The rise of anthropogenic CO<sub>2</sub> and its influence on the ocean- atmospheric interactions are well established (IPCC 2010). It is believed that such changes can influence our precipitation pattern globally and bring in other associated changes in the ecosystem. In general, the oceans act as a net sink for atmospheric CO<sub>2</sub> (Gruber et al. 2009; Takahashi et al. 2009), however, the role of coastal bodies on CO<sub>2</sub> fluxes remains unclear due to large uncertainties associated with the coastal environment (Borges et al. 2005; Cai et al. 2006; Chen and Borges, 2009; Laurelle et al. 2010). These shallow waters can modulate between net autotrophic to heterotrophic system therefore phytoplankton blooms in near shore waters has profound effect on carbon dynamics (Cloern, 1996; Chen and Borges, 2009; Merilvat and Atonie, 2014 and reference there in). Further, understanding regional pCO<sub>2</sub> fluxes associated with seasonal blooms will significantly help to reduce the uncertainties associated with the basin scale pCO<sub>2</sub> modelling.

The Bay of Bengal (northeastern Indian Ocean) is also a tropical basin similar to Arabian Sea counterpart which undergoes seasonal reversal of surface currents. It receives immense freshwater runoff from major rivers, such as the Ganges, Brahmaputra, Godavari, Mahanadi, Cauvery, Irrawaddy, and Krishna (UNESCO 1979). The fluvial inputs are major sources of nutrients to the Bay of Bengal and traditionally considered to be a region of low biological productivity because of light inhibition resulting from turbidity and cloud cover (Madhupratap et al. 2003, Prassanna Kumar et al. 2002). Earlier investigations from central Bay of Bengal exhibited pCO<sub>2</sub> less than atmospheric values in pre-southwest monsoon (Feb to late May) and northeast monsoon (November to early February) especially during the dry seasons (Sarma et al. 2012). Sarma et al. 2012 further showed lower pCO<sub>2</sub> levels in the North West region and higher pCO<sub>2</sub> levels in the South West region mainly related to the hydrological conditions such as source of fresh water discharge, residence time and quantity of organic matter in it. The enhancement of pCO<sub>2</sub> down south may presumably related to the weaker stratification and moderate upwelling which enhance pCO<sub>2</sub> further (Sarma et al. 2013).

The retrieved chlorophyll data from Ocean Colour Monitor (OCEANSAT-2) exhibited the frequent occurrence of high chlorophyll in the coastal to offshore waters of the Godavari basin, along east coast of India during pre-south west monsoon. One such enhanced chlorophyll patch was encountered during field observation between 2<sup>rd</sup> to 9<sup>th</sup> March 2012. Microscopic observation exhibited the dominance of *Skeletonema sp.* within the high chlorophyll waters. The physical events which presumably trigger such plankton blooms in this region have been recently discussed (Rao et al. 2015). However changes associated with *Skeletonema* bloom and its associated carbon dynamics

remains poorly investigated as these events are often patchy and difficult to predict (Álvarez-Salgado et al. 2005).

In this paper we evaluate one such chance observation of a diatom bloom and its influence on the pCO<sub>2</sub> variability and water column properties from coastal waters of Bay of Bengal. We also derive the primary productivity based on published carbon to chlorophyll ratio, maximum growth rate and assimilation number to gain insights in carbon sequestration by the surface waters during the bloom.

## **2.0 Materials and Methods**

### *2.1. Methodology and hydrological sampling*

This study was conducted onboard fishing trawler between 2<sup>nd</sup> to 9<sup>th</sup> March 2012, in coastal waters of Bay of Bengal within the 16°N to 17°N latitude and 82.10°E to 82.40°E longitude as illustrated in (Fig. 1). Fluorescence (Wet Labs) and Dissolved Oxygen (RINKO III, Alec Electronics Inc., Japan) sensors were integrated to Conductivity, Temperature and Depth (CTD) (Sea Bird Electronics, USA) were used to for various hydrographic measurements at each station. Sea water samples were collected at selected stations using 5 L Niskin sampler attached with nylon rope. Since it was a chance observations the transects were not clearly defined however it was ensured that more stations are sampled around the bloom area to encompass the variability associated with the bloom. Subsamples were taken for pH, Total Alkalinity (TA) and phytoplankton pigments. The pH and TA were measured using potentiometer (Metrohm, Switzerland) using Gran titration method following Standard Operating Procedures (SOP) suggested by DOE (1998). The pH electrodes were calibrated with NBS buffer solutions for pH 4.01, 7 and 9. The analytical precision was estimated to be  $\pm 0.002$  pH units determined by replicate measurements of the samples. The precision for total alkalinity was well within  $\pm 2 \mu\text{mol kg}^{-1}$ . The sea water pCO<sub>2</sub> was computed using the CO2SYS (Lewis and Wallace, 1998) program. For Pigment analysis samples were immediately filtered using Whatman GF/F (0.7  $\mu\text{m}$ , 47 mm) filters and stored -20°C and analysed within two weeks by high performance liquid chromatography (HPLC). Oxygen saturation was calculated according to standard procedures taking into account the measured temperature and salinity and oxygen concentrations and solubility of oxygen.

### *2.2. Phytoplankton pigment analysis and Microscopy*

Extraction of pigments was done in 3 ml of 100% acetone for 1 min in an ultrasonic probe (Labsonic U, B. Braun Biotech International, Leverkusen, Germany) at 50 W kept under ice to prevent excessive heating. The extracts were then stored overnight at -20°C for analysis. Entire extraction procedure was carried out in dim light and at low temperature to minimize degradation of pigments.

The high performance liquid chromatography (HPLC) analysis was carried out following the method as detailed in Roy et al. (2006). A multiple point linear calibration were made for chlorophyll c3 (chl c3), chlorophyll c1 and c2 (chlc1c2), peridinin (perid), 19' butonyloxyfucoxanthin (19' BF), fucoxanthin (fuco) , neoxanthin (neox), prasinoxanthin (prasinox), violaxanthin (violax), 19' hexanoyloxyfucoxanthin (19' HF), diadinoxanthin (diad), alloxanthin (allo), diatoxanthin (diato), zeaxanthin (zea), lutein (lutein), chlorophyll *b* (Chl*b*), chlorophyll *a* (Chl*a*) and betacarotene (b-car). Linear calibrations were performed for all compounds with a coefficient of determination ( $r^2 = 0.99$ ) for 4 point calibrations. A pre injection mixture was used where, standards and samples were mixed with 0.5 M of Ammonium Acetate in the ratio of 70:30 and 100  $\mu$ l of this mixture was injected through autosampler. The detection limit for the all the compounds varied between 0.001 and 0.002  $\mu$ g l<sup>-1</sup> and precision in terms of relative standard deviation for multiple injection of standards was well below 3 %.

For microscopic analysis samples for phytoplankton abundance and composition were fixed with 2% Lugol's iodine and stored in dark prior to microscopic examination and allowed to settled. For light microscopy, cells were examined using an Olympus BX51 inverted microscope fitted with digital camera Cells were examined live, fixed with Lugol's iodine under the magnification of 40 X and 100 X.

### 2.3 CHEMTAX Analysis

The relative abundance of microalgal groups contributing to total Chl*a* biomass was calculated by pigment concentration data using version 1.95 of CHEMTAX chemical taxonomy software (Mackey et al. 1996; Wright et al. 2000, 2010). CHEMTAX uses a factor analysis and steepest-descent algorithm to find the best fit of the data on to an initial pigment ratio matrix. The basis for calculations and procedures is fully detailed in Mackey et al. (1996). Initial pigment ratios for major algal classes were obtained from the literature (Schlüter et al. 2000; Mackey et al. 1996). Based on the diagnostic pigments detected, 4 algal groups were loaded to CHEMTAX: dinoflagellates, chlorophytes, cyanobacteria and diatoms. The pigments loaded were peridinin, fucoxanthin, violaxanthin, lutein, prasinoxanthin, zeaxanthin, chlorophyll *b*, and chlorophyll *a*. As CHEMTAX is sensitive to the feed values in the initial ratio matrix it is required to be optimized. The CHEMTAX input ratio was optimized based on (Wright et al. 2009) and the output with the smallest residual was selected further detailed in Roy et al. (2015). The input and the output ratios are given in Table I.

### 2.4. Estimation of maximum productivity during the bloom

The rates of carbon fixation at light saturation normalized to chlorophyll a is referred as the assimilation number or  $P_{\max}^B$  or productivity index usually reported in the units of grams of carbon fixed per grams of chlorophyll a per hour or per day which represent the measure of physiological state of phytoplankton.  $P_{\max}$  (maximum productivity) is defined as the product of maximum chlorophyll observed (B) and assimilation number ( $P_{\max}^B$ ). Alternately assimilation number is empirically related to maximum growth rate, phytoplankton carbon concentration and maximum chlorophyll observed at light saturation by the following equation.

$$\text{Assimilation number: } P_{\max}^B = \mu_{\max} (Cp/B) = \chi \mu_{\max} \text{ ----- (i)}$$

$\mu_{\max}$  = Maximum growth rate.

Cp= Phytoplankton carbon concentration

B = Maximum chlorophyll

$\chi$  = is carbon to chlorophyll ratio

Eppely (1972) defined the maximum growth rate as a function of temperature which is represented by the following empirical relation.

$$\mu_{\max} = 0.851 (1.066^T) \ln 2 / 24 \text{ ----- (ii)}$$

We used the average surface temperature observed during the bloom to compute the maximum growth rate ( $0.15 \text{ day}^{-1}$ ) and used the carbon to chlorophyll ratio to derive the phytoplankton productivity per day.

### 3. Results

#### 3.1 Hydrographic and biogeochemical variation

The temperature and salinity (TS) data exhibit presence of low saline water at the inshore stations with surface temperature from 27.5 to 29.5 °C and salinity varying within 31 to 32. The mixed layer was shallower at ~ 5 m at these locations which increased to ~ 10 m further offshore. In general TS properties showed marginal latitudinal variation (Fig. 2). The offshore stations show a salinity gradient of 33 to 34 PSU and exhibited similar sea surface temperature. A rapid decline in the temperature was observed below the mixed layer to reach as low as 22.0 °C at a depth of 100 m. Overall, the water column temperature ranged between 22.0 to 29.5 °C for the entire transect. The mean and ranges for temperature, salinity and other biogeochemical parameters (pH, TA, pCO<sub>2</sub>) are presented in Table II. Surface pH ranged between 8.00 to 8.17 covaried with high total alkalinity 2435 to 2495  $\mu\text{mol kg}^{-1}$ . In contrary, the bottom waters had low pH (7.80 to 7.90) and high in

pCO<sub>2</sub> with marginal increase in total alkalinity. The oxygen data collected during the investigation suggest varying degree of saturation (Fig. 2). Within the top 5 m the oxygen saturation varied between 100 to 116% but decreased sharply below the mixed layer to reach as low as 6 % at a depth of 100 m. The rapid gradient observed oxygen saturation coincides with the halocline depth. In general surface waters were high in oxygen and low in pCO<sub>2</sub> (287 to 479 μatm) however pCO<sub>2</sub> increased sharply below the mixed layer to reach as high as 600-800 μatm (Fig. 2).

### 3.2 Spatial variability of phytoplankton pigments and microscopic cell counts in coastal waters of Bay of Bengal

The major pigments observed were the chlorophylls: chlorophyll *a*, chlorophyll *b*; the photosynthetic carotenoids (PSC): fucoxanthin and peridinin and the photoprotective carotenoids (PPC): diadinoxanthin, diatoxanthin, zeaxanthin, betacarotene. The suite of marker pigments suggest that the phytoplankton community was dominated by diatoms, chlorophyll *b* containing green algae, cyanobacteria with minor contribution from peridinin containing dinoflagellates. Highest chlorophyll *a* concentrations coincided with a bloom of *Skeletonemacostatum* as observed by the OCM 2 sensor (Fig. 1). Highest surface chlorophyll concentrations recorded was 4.114 μg l<sup>-1</sup> and had a range between 0.360 to 4.114 μg l<sup>-1</sup>. The spatial variability of specific marker pigments is illustrated in (Fig. 3). Phytoplankton cell counts of surface waters from selected stations showed dominance of diatoms (Fig. 4). *Skeletonemacostatum* and *Chaetoceros* sp. were the main diatom population observed which together contributed greater than > 90 % of the total cell count. Surface waters collected from the bloom area recorded a total cell of 36898 per liter where in *Skeletonemacostatum* contributed ~ 71 % to the total phytoplankton cells. Overall only five diatom species were dominant during the entire period (*Skeletonemacostatum*, *Chaetoceros* sp., *Guinardia flaccida*, *Nitzschia longissima* and *Nitzschia sigma*) with minor presence of dinoflagellates (*Ceratium tripos*, *Ceratium furca* and *Peridinium* sp) other species such as *Trichodesmium erythraeum* and green algae *Enteromorpha intestinalis*.

The relative contribution of various phytoplankton groups to Chl *a*, was analyzed by CHEMTAX (Fig. 5) which identified presence of chlorophytes, cyanobacteria, diatoms and dinoflagellates. Diatoms (av.=1.234) were the dominant group during the entire transect and contributed 32-98 % to Chl *a* biomass followed by modest presence of chlorophytes (av.=0.233 μg l<sup>-1</sup>) specially at the southern end. Groups such as cyanobacteria (av.=0.034 μg l<sup>-1</sup>) and dinoflagellates (av.=0.018 μg l<sup>-1</sup>) were occasionally detected representing < 5 % of the background population. CHEMTAX data showed dominance of mixed assemblage (chlorophytes and diatoms) at the southern end with gradual community shift to diatoms at north. Phytoplankton cell counts of surface waters from selected stations are well corroborated with CHEMTAX analysis (Fig. 5). *Skeletonemacostatum* and

*Chaetoceros* spp. were the main diatom population observed which together contributed greater than > 90 % of the total cell count. Surface waters collected from the bloom area recorded a total cell of 36898 per liter where in *Skeletonemacostatum* contributed ~ 71 % to the total phytoplankton cells. Overall only five diatom species were dominant during the entire period (*Skeletonemacostatum*, *Chaetoceros* sp., *Guinardia flaccida*, *Nitzschia longissima* and *Nitzschia sigma*) with minor presence of dinoflagellates (*Ceratium tripos*, *Ceratium furca* and *Peridinium* sp.) other species such as *Trichodesmium erythraeum* and green algae *Enteromorpha intestinalis*.

#### 4. Discussion

Coastal waters represent 7 % of the global ocean (Borges, 2005) but accounts for 14 to 30 % of the oceanic primary production making it an important site to investigate marine carbon cycle (Gattuso et al. 1998; Muller-Karger et al. 2005). Bay of Bengal receives large quantity of fresh water from the major rivers such as Ganges, Brahmaputra, Mahanadi, Godavari, and Krishna leading to low surface salinity and strong stratification (Shetye et al. 1996; Howden and Murtugudde, 2002; Vinayachandran et al. 2002; Sengupta et al. 2006; Sarma et al. 2009 as observed here (Fig. 2). Riverine run off can often be the source of nutrients in the coastal ocean hence can modulate phytoplankton community structure with short burst of phytoplankton blooms as observed during this investigation. The time of this study overlaps with a modest bloom of *Skeletonemacostatum* as identified microscopically. The high chlorophyll filaments and the spatial extent of the bloom as observed by Ocean Colour Monitor-2 (Oceansat-2) data is presented in (Fig. 1) which suggest a maximum increase of  $3.5 \mu\text{g l}^{-1}$  of chlorophyll *a*. This is very close to the in situ measured surface chlorophyll of  $4.114 \mu\text{g l}^{-1}$  taking into consideration the large errors often associated with phytoplankton blooms and with satellite measured chlorophyll *a* (Nagamani et al., 2013). Our microscopic observation and pigment analysis suggest high abundance of diatoms in the water column. In general fucoxanthin was the major marker pigment observed with presence of diatoxanthin and diadinoxanthin. Lack of 19' butynoyloxyfucoxanthin and 19' hexanoyloxyfucoxanthin confirms fucoxanthin was contributed from diatoms and not prymnesiophytes. CHEMTAX analysis suggests modest presence of chlorophytes in the south with gradual shift to diatoms in north. This change observed in conjunction with low surface values of  $\text{pCO}_2$  suggests strong biological influence. Traditionally Bay of Bengal is considered as low productive as most of the riverine inputs are recycled within the estuary itself (Prasanna Kumar et al. 2002; Sarma et al. 2009; 2013). We speculate that bloom of *Skeletonemacostatum* in this region presumably coincide with the beginning of the coastal upwelling which brings in nitrate and phosphate within the mixed layer which is already rich in silicate (Sarma et al. 2012) between March

to May. The East Indian Coastal Current which reverse their direction this time flows northeastward with a strong peak between March-May (Schott and McCreary, 2001) presumably brings in nutrients to the surface (Wiggert et al. 2005; Levy et al. 2007) which is otherwise oligotrophic (Rao et al. 1994).

The lowest surface pCO<sub>2</sub> of 287 µatm was observed at the southern end of the transect associated with chlorophyll *a* concentrations of 1.090 µg l<sup>-1</sup>. The population here comprised of both chlorophytes and diatoms. Within the diatom bloom (on the northern side), surface pCO<sub>2</sub> went as low as 313 µatm in conjunction with high chlorophyll concentration of 4.114 µg l<sup>-1</sup>. Such natural pCO<sub>2</sub> modulation has been earlier observed in Southern Ocean and in mesocosm experiment (Arrigo et al. 1999; Schippers et al. 2004; Tortell et al. 2008; Riebesell et al. 2000; 2004) and more recently within fronts and filaments from the Arabian Sea (Sarma et al. 2015). Sharp decline in oxygen saturation (< 50 %) were observed at near bottom depths coinciding with the high saline barrier layer often observed in Bay of Bengal (Sardesai et al., 2007). pCO<sub>2</sub> concentration in this layer increased upto (~ 600 µatm) roughly twice of that of surface values. The lowest oxygen saturation covaried with low pH, high TA and elevated pCO<sub>2</sub> indicative of active community respiration. However except for brief north east monsoon (February to April) coastal Bay of Bengal act as a net source to atmospheric CO<sub>2</sub> influenced greatly by riverine waters (Sarma et al. 2012), therefore blooms such as this can significantly influence the net exchange on shorter time scales. During this study significant low pCO<sub>2</sub> was observed till a depth of 10 m.

The scatter plots showing the various relationships between hydrographic parameters and pCO<sub>2</sub> are illustrated in (Fig. 6). High surface chlorophyll associated with low pCO<sub>2</sub> presumably suggest that surface waters was acting as a sink (through primary production) however weak coefficient of determination ( $r^2$ ) between chlorophyll *a* and pCO<sub>2</sub> (Fig. 6) highlights interplay of complex mechanism. For instance, Increase in chlorophyll-*a* within the surface mixed layer may presumably enhanced CO<sub>2</sub> draw down causing shift in equilibrium and direction of fluxes however this can only explain ~1/4<sup>th</sup> of the pCO<sub>2</sub> variability in our data as observed from the low correlation between pCO<sub>2</sub> and chlorophyll *a*. Various physico-chemical factors can influence the surface pCO<sub>2</sub> concentrations such as carbonate equilibrium, physical mixing of different water mass, different stages of bloom and microbial process resulting in weak correlation such as this. Relationship between temperature and pCO<sub>2</sub> was also negative but statistically significant ( $r = 0.63$ ,  $p < 0.01$ ,  $n = 64$ ). This suggests low temperature waters were associated with high pCO<sub>2</sub>. However salinity exhibited weak positive correlation with pCO<sub>2</sub> indicating minor riverine influence. These relationships clearly mimics broad trends observed from Godavari estuary (Sarma et al. 2012). Although CHEMTAX analysis clearly



indicates community shifts from south to north concomitant with drop in pCO<sub>2</sub> such is not reflected in the scatter plots which shows weak relationships with the dominant groups. This suggest complex interplay of physical and biological factors leading to low pCO<sub>2</sub> in the surface water.

We used the published C:Chl-*a* ratio for *Skeletonemacostatum*(Han et al. 1994) to gain some insights into carbon dynamics and get a modest idea of carbon sequestration in the surface waters in terms of per microgram of chlorophyll *a* synthesized. It must be noted this ratio is highly variable since it depends on the physiological state of the phytoplankton and environmental condition of the water column. To come up with a modest number we averaged the C:Chl ratio to 27 based on the range of data observed by (Han et al. 1994) during a bloom of *Skeletonemacostatum* in Tokyo Bay. The product of surface chlorophyll and the ratio was used to understand the carbon sequestered per microgram of chlorophyll *a* and to derive the phytoplankton productivity. This varied from 10 to 113 µg of carbon with an average of 56 µg per microgram of carbon per microgram of chlorophyll *a*. The primary productivity derived from maximum growth rate and assimilation number and maximum surface chlorophyll yielded a modest number of 160.6 mg C m<sup>-2</sup>day<sup>-1</sup>. This is on the lower side compared to earlier observation from Bay of Bengal that ranged from 40 to 500 mg C m<sup>-2</sup>day<sup>-1</sup> (Madhupratap et al. 2003). This difference presumably linked to the low growth rates yielded based on the equation proposed by Eppley (1972). The product of spatial extent of this bloom observed from the satellite data on 7<sup>th</sup> March 2012 and derived surface primary production suggest ~ 0.08 Gg of carbon was sequestered per day. Eventhough we believe there is uncertainties involved in these assumptions the numbers however indicates the potential role of these bloom in coastal waters and it's profound influence on carbon dynamics when extrapolated spatially.

## Conclusions

A bloom of diatom *Skeletonemacostatum* was monitored to understand its role in influencing pCO<sub>2</sub> dynamics in coastal waters of Bay of Bengal. Significant draw down of pCO<sub>2</sub> was observed within the 10m water column covarying with high chlorophyll *a* concentration and *Skeletonemacostatum* cell counts. The lowest pCO<sub>2</sub> of 287 µ atm was encountered at the southern end of the transect where chlorophyll *a* concentrations was 1.09 µg l<sup>-1</sup>. In the vicinity of the bloom area surface pCO<sub>2</sub> lowered to 313 µ atm in conjunction with high chlorophyll. The product of spatial extent of this bloom observed from the satellite data and derived surface primary production showed modest sequestration of 0.08 Gg of carbon per day. This investigation highlights that coastal blooms play a critical role in influencing local pCO<sub>2</sub> dynamics where diatoms supersede other groups due to the large surface area and high sinking rates. With the rapid decline in the oceanic pH due to anthropogenic activities makes coastal phytoplankton population more susceptible as any shifts in the natural community

assemblage may influence the local pCO<sub>2</sub> dynamics in the coastal ocean and natural carbon sequestration

### **Acknowledgements**

This work was carried out as a part of the National Carbon Project (NCP) of ISRO-IGBP. Authors would like programme director ISRO IGBP and Chairman ISRO for their constant encouragement and support. PL would like to thank ISRO for her research support.

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## Figure Legends

**Figure 1:** Sampling locations (1a) along the south west coast of India (1b) satellite data from OCM2 showing increasing in chlorophyll biomass due to the proliferation of *Skeletonema* along the south coast of India.

**Figure 2:** Spatial distribution of (a) temperature ( $^{\circ}\text{C}$ ), (b) salinity (psu), c) pH, d) TA ( $\mu\text{Mol kg}^{-1}$ ) e) DO saturation (%) f)  $\text{pCO}_2$  ( $\mu\text{atm}$ ) during the *Skeletonema* bloom observed along the south west coast of India.

**Figure 3:** Distribution of HPLC measured various marker pigments (a) chlorophyll *a* ( $\mu\text{g l}^{-1}$ ), (b) fucoxanthin-diatoms ( $\mu\text{g l}^{-1}$ ), (c) chlorophyll *b*- green algae ( $\mu\text{g l}^{-1}$ ), (d) peridinin-dinoflagellates ( $\mu\text{g l}^{-1}$ ) (e) zeaxanthin-cyanobacteria ( $\mu\text{g l}^{-1}$ ) during March 2012.

**Figure 4:** Surface variability of total phytoplankton cells, diatoms and dinoflagellates along south west coast of India as revealed by microscopic analysis (of cells  $>20 \mu\text{m}$ ).

**Figure 5:** Relative percentage contribution of main phytoplankton groups to Chlorophyll *a*, as estimated by interpretation of pigment HPLC data using the CHEMTAX program in  $\mu\text{g l}^{-1}$ .

**Figure 6:** Scatter plots showing the various relationships observed between water column  $\text{pCO}_2$  and CHEMTAX derived phytoplankton groups and physical parameters (T, S).

**Table I**

Marker pigments to Chlorophylls. A) Input ratios were obtained from (Schlüter et al. 2000; Mackey et al. 1996). B) Estimated output ratios based on CHEMTAX program.

<b>A) Input Ratios</b>							
Class/Pigments	perid	fucox	prasincox	violax	zeax	chl_b	chl_a
Prasinophytes	0	0	0.057	0.011	0	0.172	1
Dinoflagellates	0.391	0	0	0	0	0	1
Chlorophytes	0	0	0	0.002	0.004	0.591	1
Cyanobacteria	0	0	0	0	0.512	0	1
Diatoms	0	0.651	0	0	0	0	1
<b>B) Output Ratios</b>							
Class/Pigments	perid	fucox	prasincox	violax	zeax	chl_b	chl_a
Prasinophytes	0	0	0.079	0.015	0	0.238	1
Dinoflagellates	0.513	0	0	0	0	0	1
Chlorophytes	0	0	0	0.017	0.02	0.59	1
Cyanobacteria	0	0	0	0	0.371	0	1
Diatoms	0	0.432	0	0	0	0	1

**Table II:** Water column (~ 75 m) mean concentration of various physico-chemical parameters as observed during the bloom of *Skeletonemacostatum* along east coast of India.

Stn No	Lat	Long	pH	TA ( $\mu\text{mol kg}^{-1}$ )	Temp ( $^{\circ}\text{C}$ )	Sal (PSU)	pCO <sub>2</sub> ( $\mu\text{atm}$ )
1	16.71 07	82.42 13	8.111 $\pm$ 0.07	2445 $\pm$ 9	28.73 $\pm$ 0.71	33.08 $\pm$ 0.43	344 $\pm$ 180
2	16.70 52	82.43 65	8.053 $\pm$ 0.14	2464 $\pm$ 13	27.52 $\pm$ 0.78	33.81 $\pm$ 0.24	436 $\pm$ 311
3	16.68 54	82.44 96	8.021 $\pm$ 0.12	2474 $\pm$ 37	25.44 $\pm$ 1.75	34.21 $\pm$ 0.76	312 $\pm$ 226
4	16.75 73	82.41 36	7.961 $\pm$ 0.08	2302 $\pm$ 628	23.64 $\pm$ 6.27	31.81 $\pm$ 0.64	522 $\pm$ 232
5	16.82 32	82.42 29	7.883 $\pm$ 0.14	2485 $\pm$ 36	24.11 $\pm$ 2.07	34.82 $\pm$ 0.06	517 $\pm$ 169
6	16.87 99	82.46 47	8.042 $\pm$ 0.13	2474 $\pm$ 17	27.32 $\pm$ 1.15	33.66 $\pm$ 0.30	692 $\pm$ 173
7	16.87 49	82.53 12	8.011 $\pm$ 0.12	2538 $\pm$ 105	25.66 $\pm$ 2.43	34.19 $\pm$ 0.71	448 $\pm$ 205
8	16.91 69	82.48 72	8.031 $\pm$ 0.14	2458 $\pm$ 20	26.28 $\pm$ 2.16	34.22 $\pm$ 0.78	501 $\pm$ 173
9	16.95 19	82.42 09	7.804 $\pm$ 0.34	2633 $\pm$ 343	27.25 $\pm$ 0.82	33.65 $\pm$ 0.56	463 $\pm$ 205
10	16.85 50	82.46 37	7.96 $\pm$ 0.11	2479 $\pm$ 21	25.97 $\pm$ 1.71	34.17 $\pm$ 0.55	1094 $\pm$ 961
11	16.79 14	82.49 01	7.983 $\pm$ 0.14	2495 $\pm$ 15	25.17 $\pm$ 2.23	34.26 $\pm$ 0.50	556 $\pm$ 160
12	16.75 33	82.51 45	7.910 $\pm$ 0.09	2485 $\pm$ 35	25.12 $\pm$ 2.95	34.33 $\pm$ 0.61	634 $\pm$ 153

Figure 1

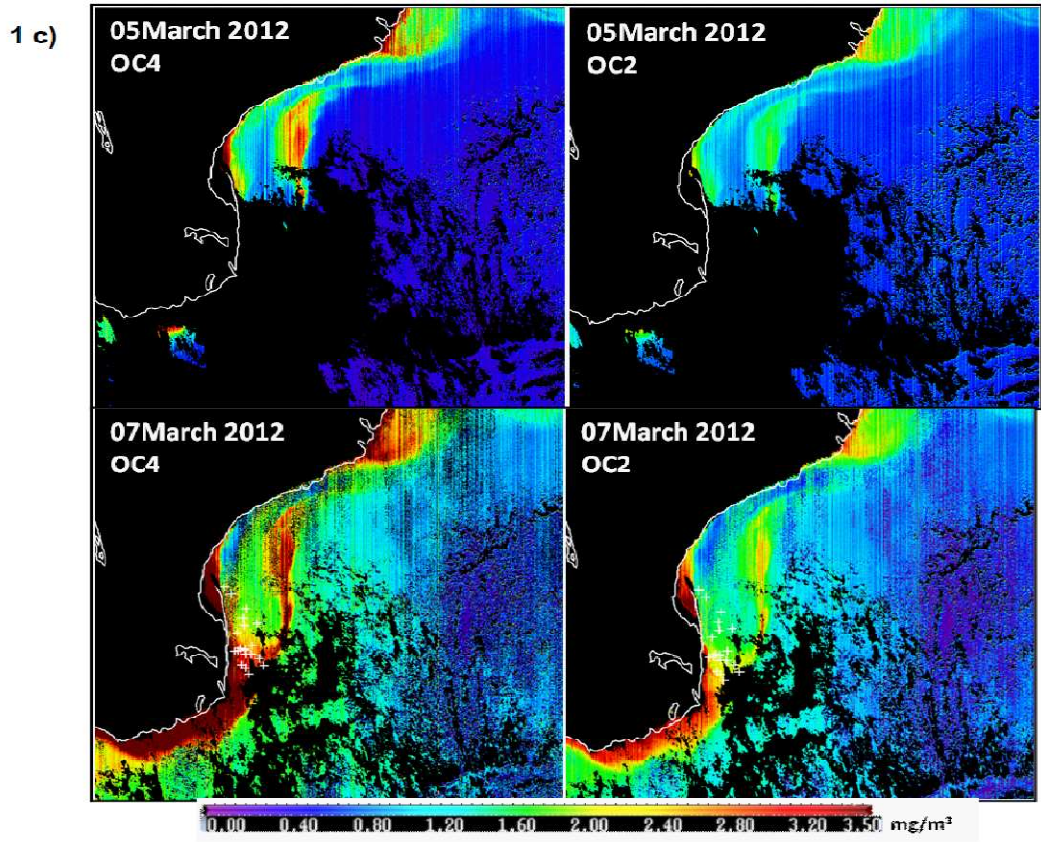
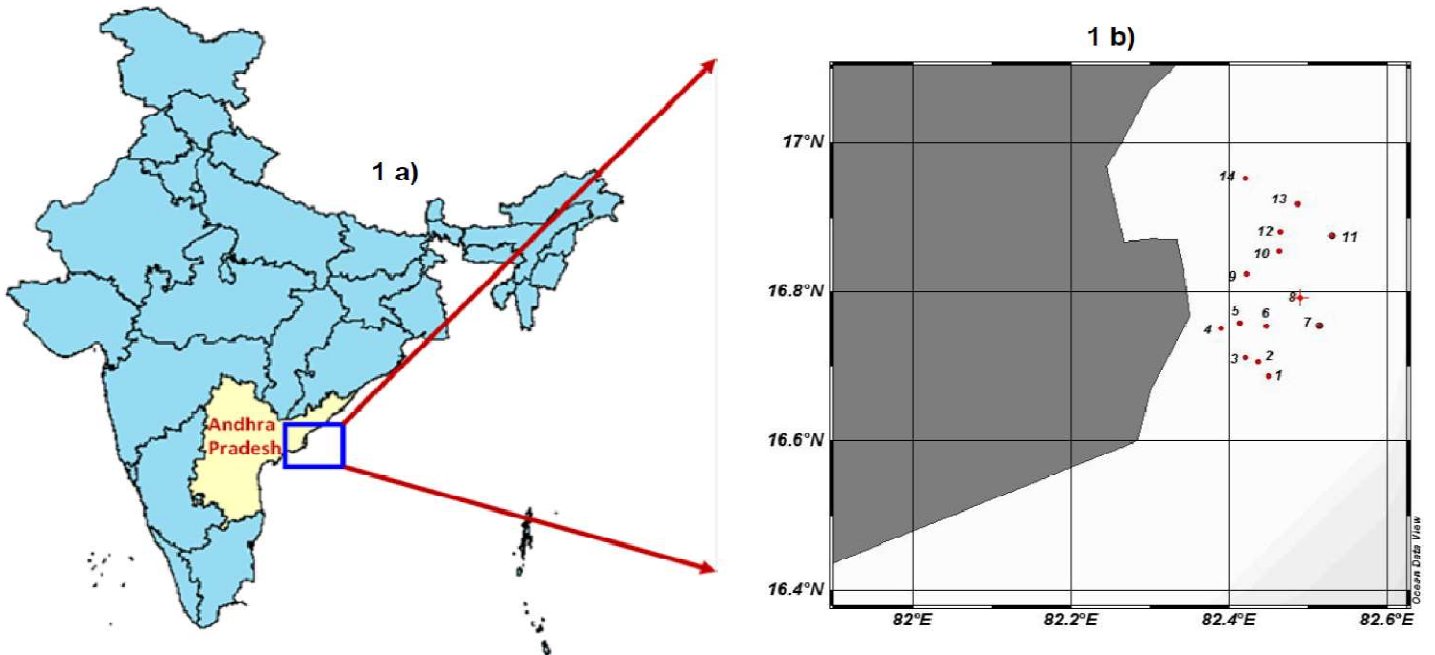




Figure 2

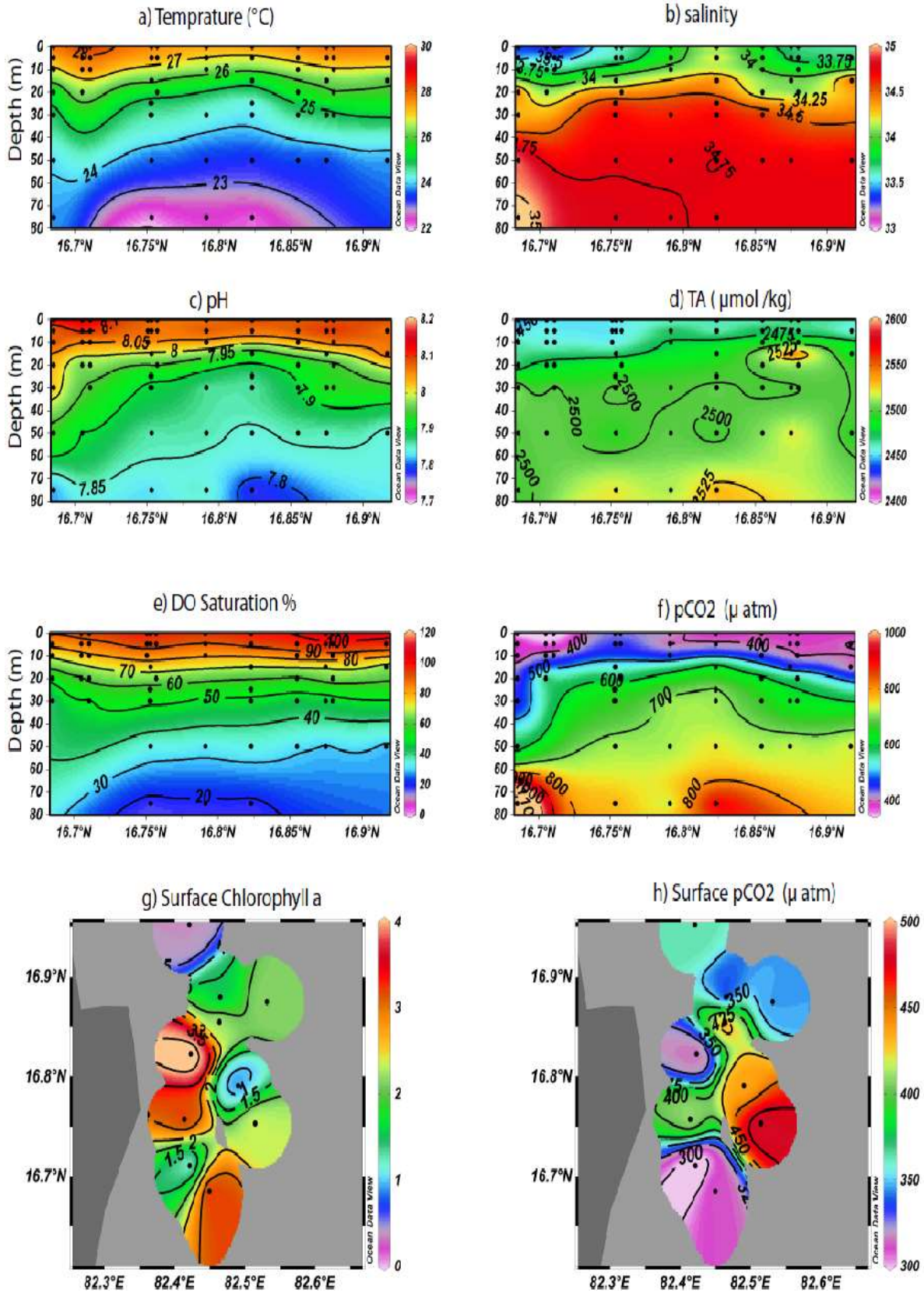


Figure 3

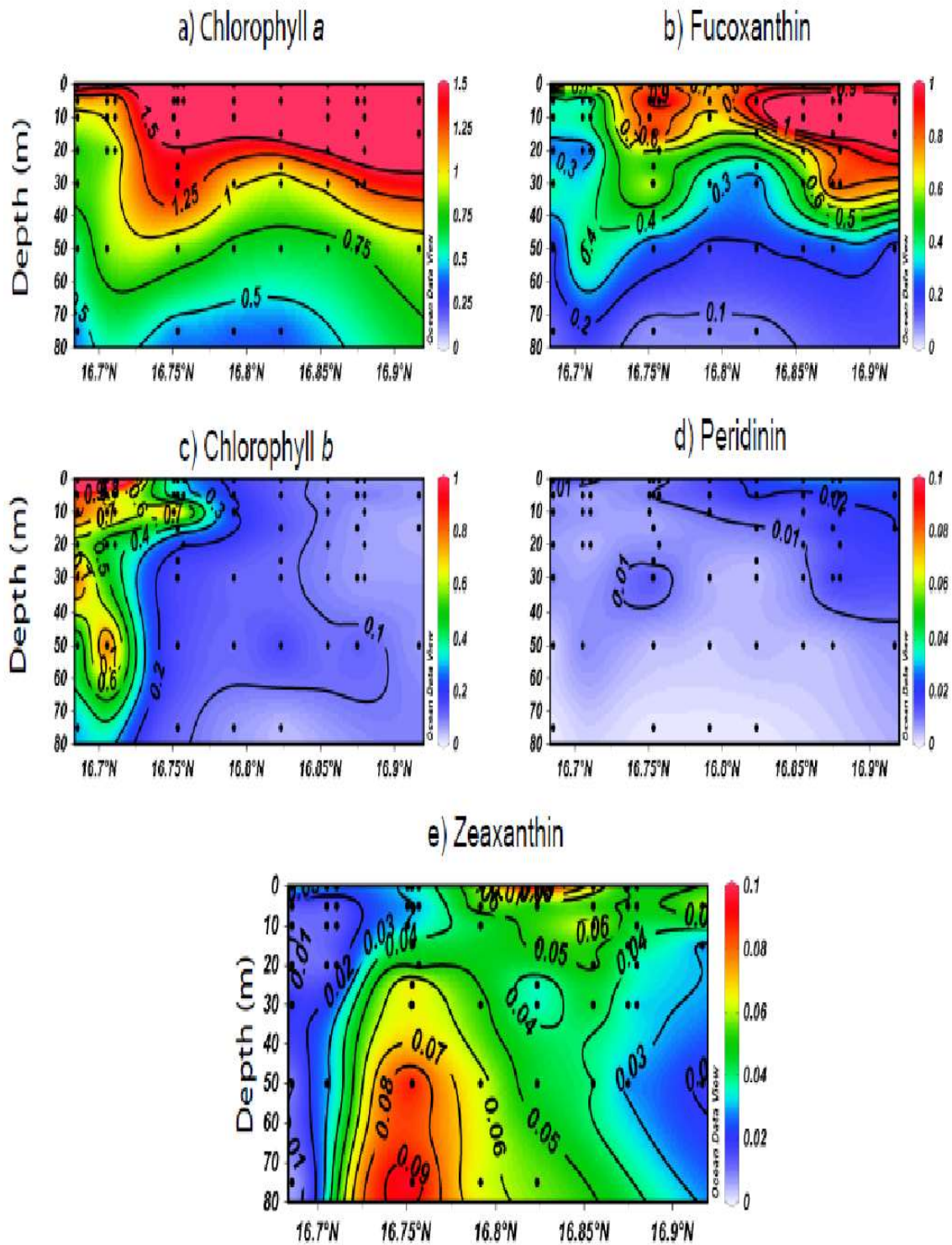
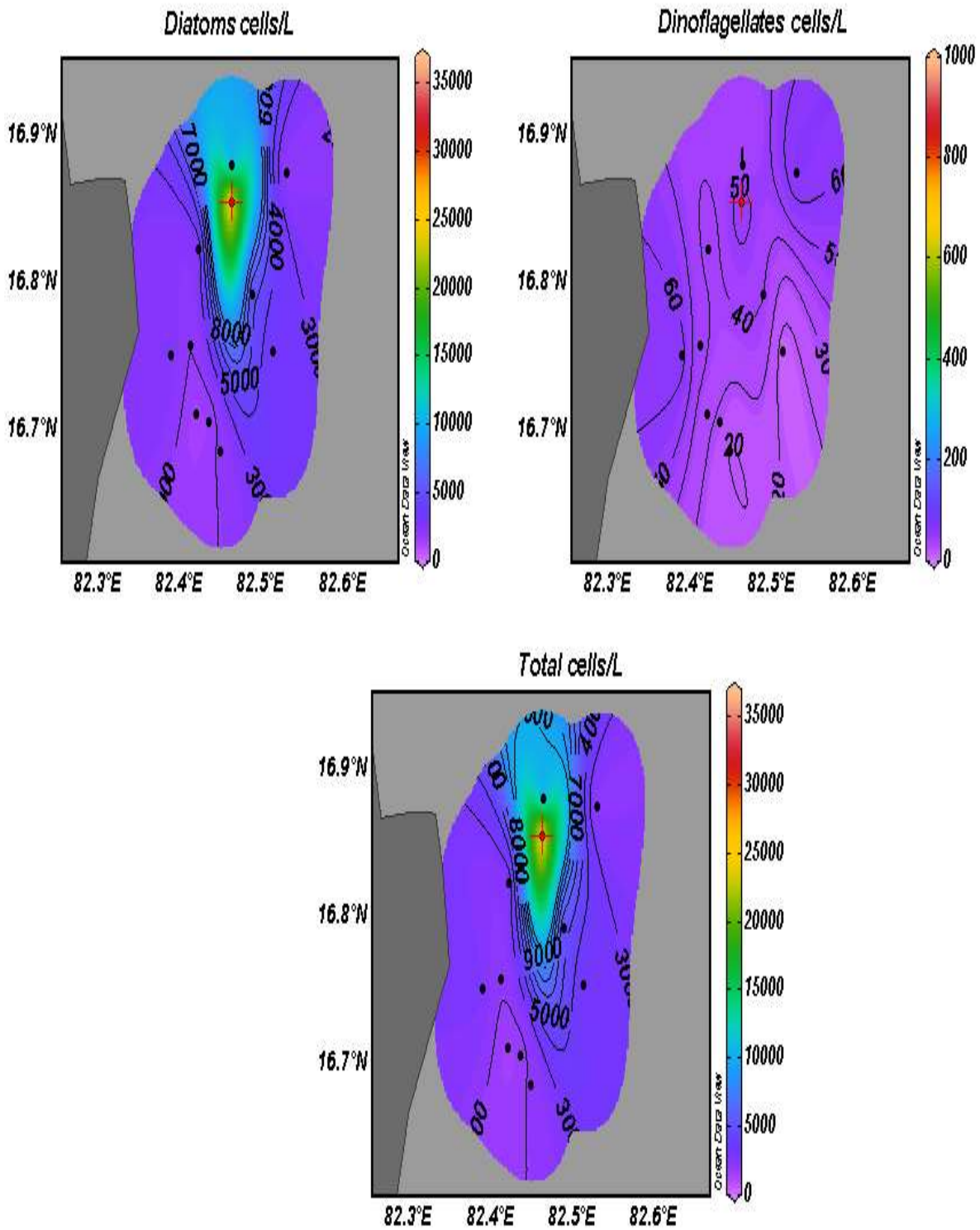


Figure 4



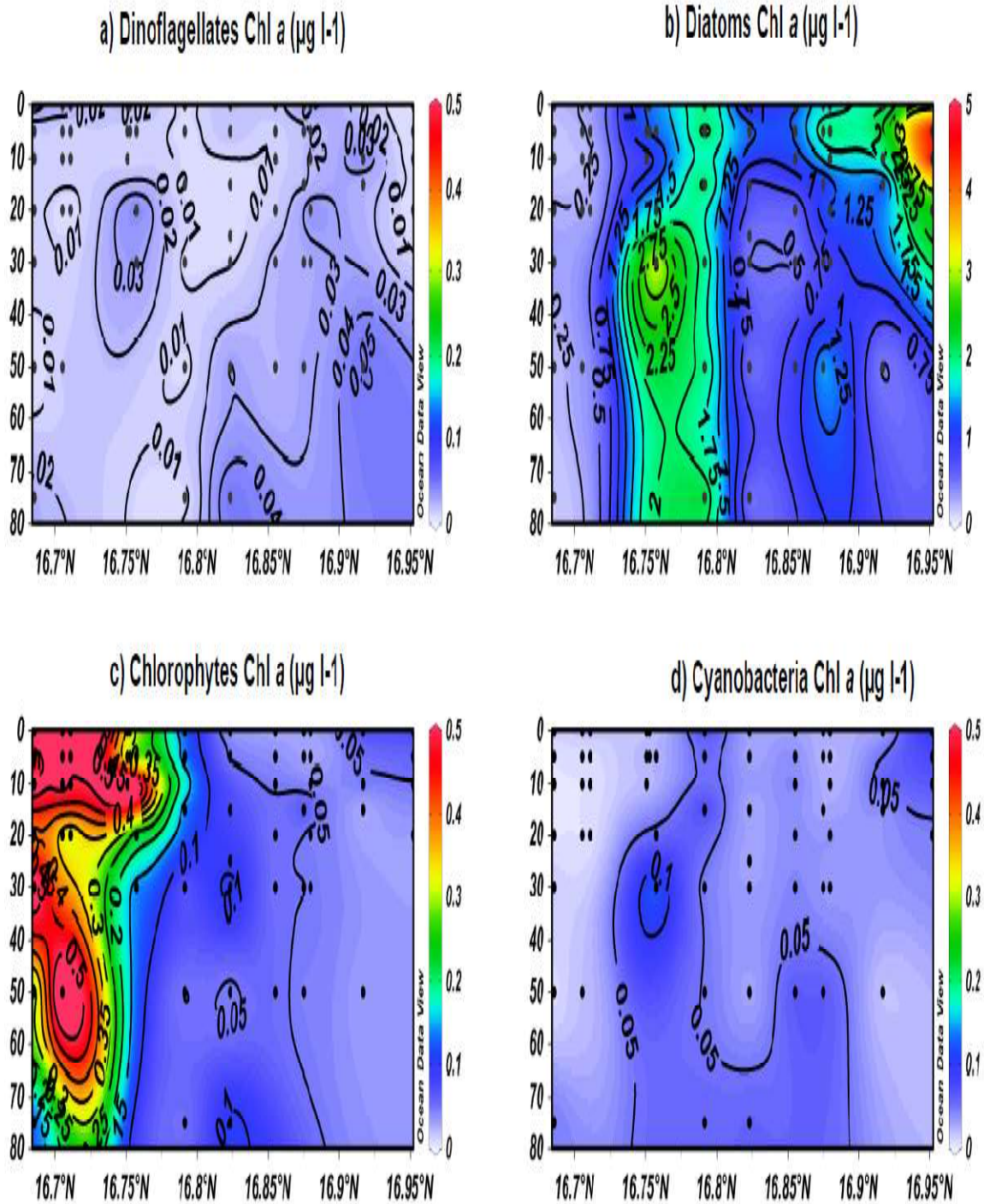


Figure 5

Figure 6

