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Temporal Variability of Size-fractionated Chlorophyll *a* Concentration and Influence of Chemical Parameters in Coastal waters of South-eastern Arabian Sea

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Abstract

Phytoplankton size structure influences the underwater light field and determines the fate of carbon in a pelagic food chain. Temporal and vertical variations of size fractionated chlorophyll a concentration (Chl-a) were investigated along coastal region off Kochi from May 2013 to April 2014 in order to understand the influence of environmental parameters on phytoplankton size distribution in coastal waters of South-eastern Arabian Sea. The study identified abundance of microphytoplankton around 10m depth, nanophytoplankton from surface to 5m depth and picophytoplankton in 10-20m water column. The results also showed that increased nitrate and phosphate concentration favoured nanophytoplankton growth and increased silicate concentration favoured the growth of microphytoplankton. Pre-showers and extended southwest monsoon along with variation in nutrient concentrations in the area during the study period significantly influenced the variation in size fractionated chlorophyll, absorption by phytoplankton and its numerical density. The results will provide an insight into the chemical factors that control the production cycle in this neritic system and can be used to improve the size fraction algorithms for various societal applications of remote sensing.

Keywords: Phytoplankton, Size fraction, Chlorophyll, Arabian Sea

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Introduction

Understanding the spatio-temporal variability of community structure in a water column is critical to evaluate the relationship between environmental parameters and phytoplankton size distribution. The phytoplankton size distribution is mainly expressed in terms of chlorophyll a (Alvarez-Fernandez & Riegman, 2014). Phytoplankton size structures are the result of success of certain community to survive and grow in an unstable environment controlled by varying physical and chemical characteristics. Dominance of a particular phytoplankton in euphotic layer depends on its ability to resolve problems related to floatability, uptake of nutrients, growth and grazing by herbivores (Rodriguez & Guerrero, 1994). Apart from that, in recent research of oceanography, based on ocean colour remote sensing, it was found that phytoplankton size structure significantly affects optical properties of surface waters. The main optical property used to distinguish phytoplankton communities is its spectral absorption (Ciotti et al., 2002).

Cochin coast located in the South-eastern Arabian Sea has a strong monsoonal influence resulting in seasonal changes in hydrographic conditions (Minu, et al., 2014a, 2014b). During pre-monsoon (February-May) wind-induced upwelling along with a northward undercurrent and a southward surface flow is associated with strong vertical mixing in this area (Kumar & Kumar, 1996). During monsoon period very high production is noted at primary and secondary levels due to the increase in nutrients and detrital load, decrease in salinity and water temperature and diminished light penetration. After monsoon season, the hydrographic parameters change causing very strong fresh water discharge from backwaters (Srinivas & Kumar, 2006).

Several models and approaches have been developed for deriving information about cell size from phytoplankton absorption spectra (Brewin et al., 2011). The cell size of phytoplankton is crucial, as the absorption of light by large phytoplankton cells are influenced by packaging effect (Baird et al., 2007; Bricaud et al., 1995; Sathyendranath et al., 1987). Satellite ocean colour data has been used in several approaches to differentiate phytoplankton cells based on their cell size (Brewin et al., 2010; Ciotti & Bricaud 2006; Ciotti et al., 2002; Devred et al., 2006). These approaches have been validated on global scale but regional validation and adaptation is needed since phytoplankton communities are influenced by the local specificities of their environment (Brito et al., 2015; Minu et al., 2014b). Hence a study was carried out to understand the temporal and vertical variability in size fractionated chlorophyll *a* (Chl a) and to understand the influence of environmental parameters on phytoplankton size distribution in coastal waters of South-eastern Arabian Sea for the year 2013- 2014. These data will provide an insight into the chemical factors that control the production cycle in this neritic system. General pattern in the size structure of the phytoplankton community were also investigated.

Materials and Methods

Water samples were collected on monthly basis from 8 stations along 10m and 20m bathymetry (Fig. 1) during May 2013 to April 2014 using a commercial vessel. The depth at the sampling site varied from 5-20m. Samples collected using Niskin water sampler and clean bucket (for surface samples) were stored in dark polyethylene bottles and kept in ice and transported to the laboratory where further analysis was carried out. Turbidity was measured using Nephelometer (NTU) (Micro 100 IR), water temperature (°C) with tester (Eutech pH 30 tester) and pH with digital pH meter (Eutech pH 30 tester). Salinity and Dissolved Oxygen (DO) were determined by titration method (Grasshoff et al., 1983). Concentrations of nutrients like nitrite, nitrate, phosphate, silicate and ammonia were measured using spectrophotometer according to standard protocols (Grasshoff et al., 1983). Total Suspended Matter (TSM) concentration determined according to Strickland & Parsons (1972) and JGOFS protocols (UNESCO, 1994).

Water samples were filtered using a manifold and a vaccum pump to obtain **i**) the total chlorophyll

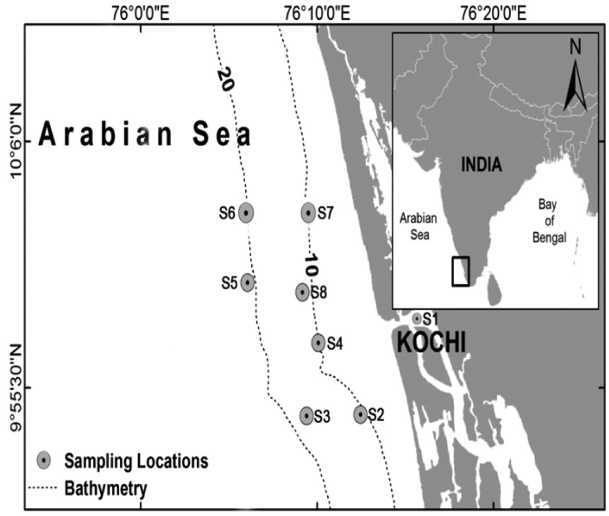

Fig. 1. Study area with bathymetry and stations

concentration, filtered through Whatmann GF/F membrane filters (0.7 μm pore size) and **ii**) the fraction > 20mm were first sieved by gravity through 20 μm nylon mesh on top of Whatmann GF/F membrane filters (Rodriguez & Guerrero, 1994; Arin et al., 2002). The filtrate was passed subsequently through GF/F membrane filters of 0.7 μm pore size and nylon membranes of pore size 0.2 μm, in order to get the size fractions 0.7-20 and 0.2-0.7 μm. Pigment determination wasd one after solvent extraction (90% acetone) and then quantified in a fluorometer (10 AU Turner Design) (Kishino et al., 1985). Calibration was done with standard chlorophyll-a (Sigma, USA). Temporal variation represented using Ocean Data Viewer (ODV ver. 4.2)

Results and Discussion

Monthly variations in total chlorophyll concentration are showed in Fig. 2. Chlorophyll concentration of total phytoplankton (Chl_{total}) was high during May, January and April in the surface waters of estuarine side. Horizontal and vertical variability was prominent during August, November and December. Vertical and horizontal variation of chlorophyll concentration for microphytoplankton (Fig. 3) was minimal during May, September, and from November to April. But during August and October, vertical variability was prominent and horizontal variability was minimal. During August, the concentration ranged from 0-20 mg m^{-3}. Very high $Chl_{micro}$was measured in 5 to 20m depth water column between 76.15E (S3, S4) and 76.25E (S1) during the month. Similar condition was observed in the month of October also. During the month of October, there was no sharp vertical variability and the concentration reached only upto 7mg m^{-3}. In the month of March, high $Chl_{micro}$was observed towards the estuarine part due to presence of *Trichodesmium* bloom. The contribution of microphytoplankton was more towards 10m depth.

Variations in chlorophyll concentration of nanophytoplankton (Chl_{nano}) are shown in Fig. 4. Chl_{nano} showed vertical variation in the surface waters to 5m during May 2013. High concentration was measured in the surface waters towards estuarine side and low concentration in the bottom waters. During August, eventhough vertical gradient was exhibited; the concentration did not reach as high as Chl_{micro}. The maximum Chl_{nano} measured was only 5 mg m^{-3}. Other months exhibited Chl_{nano} between 0-2mg m^{-3}. During October, comparatively higher Chl_{nano} was measured around 20m depth along 76.15E longitude. Similar condition was observed in the bottom waters of estuarine station during December 2013. Nanophytoplankton was mainly concentrated in the surface to 5m depth.

The chlorophyll concentration of picoplankton (Fig. 5), Chl_{pico} seemed to be the least contributors. August, September and October are the favouring season for picoplankton growth. During these months Chl_{pico} reached upto 1mg m^{-3} while in other months it reached only upto 0.4mg m^{-3}. High vertical variability was observed in October. Chl_{pico} was measured high in water column between 10 and 20m depth.

High numerical density of phytoplankton was measured during September 2013. In September 80% of the total numerical density was contributed by *Biddulphia* cells which had undergone cell division; followed by *Coscinodiscus* spp. and *Fragilaria* spp. Small sized cells (<0.2 μm) were observed during October 2013. The regression analysis showed that total chlorophyll concentration is in good agreement with the sum of chlorophyll concentration measured in different size fractions (R^2=0.87; N=81) (Fig. 6).

The concentration of nutrients *viz.,* Nitrite, Nitrate, Ammonium, Phosphate and Siliate are shown in the Table 1. The estuarine station exhibited high concentration of nitrite in the surface waters during May. The vertical variability in nitrite concentration was observed in August. Concentrations between 3.5 and 4.0 μmol L^{-1} was measured in 20m depth. In September, high nitrite concentrated waters are pushed upwards making the vertical variability in surface waters sharp mainly in the coastal waters. During October, low nitrite concentrated waters from estuarine side pushed waters with high concentration towards off shore and downwards and in November, low nitrite waters dominated in the study area.

Nitrate concentration showed an inverse variability with depth in May. In the coastal stations low concentration of nitrate was measured from the surface to bottom. In August an increase in nitrate concentration along with increase in depth in coastal waters was observed. The whole study area showed very low nitrate concentration in the month of September. October had nitrate concentration between 6-8 μmol L^{-1} in most of the stations. Not much horizontal and vertical variation in nitrate concentration was measured during November.

May to September had ammonium concentration between 0-6 μmol L^{-1}. In October, surface waters showed high ammonium concentration than bottom waters. A vertical gradation was observed during October. During November high ammonium was noticed only in the surface waters of estuarine station. All other study area showed concentration between 0-6 μmol L^{-1}. Vertical variability was observed in November in the estuarine station. Concentration between 6-12 μmol L^{-1} was observed in waters between 5-20 m water columns.

The phosphate concentration were below detectable limits in August. During May the concentration was lower in the coastal waters than estuarine waters. Towards estuarine side the concentration was between 1-1.5 μmol L^{-1}. The surface waters exhibited phosphate conccentartion between 0.5-1 μmol L^{-1} while in 5-10m water column the concentration was between 1-1.5 μmol L^{-1} during October. The 10-15m water consisted of phosphate concentration in the range 1.5-2 μmol L^{-1}.

During August and September silicate concentration varied between 10-25 μmol L^{-1}, while during October, silicate concentration reduced, with comparatively high concentration in the coastal waters. Concentration between 0-5 μmol L^{-1} was measured in 5 m depth and estuarine station. In November, very low silicate concentration was confined only to the surface waters. Most of the study area was under silicate concentration 5-10 μmol L^{-1}.

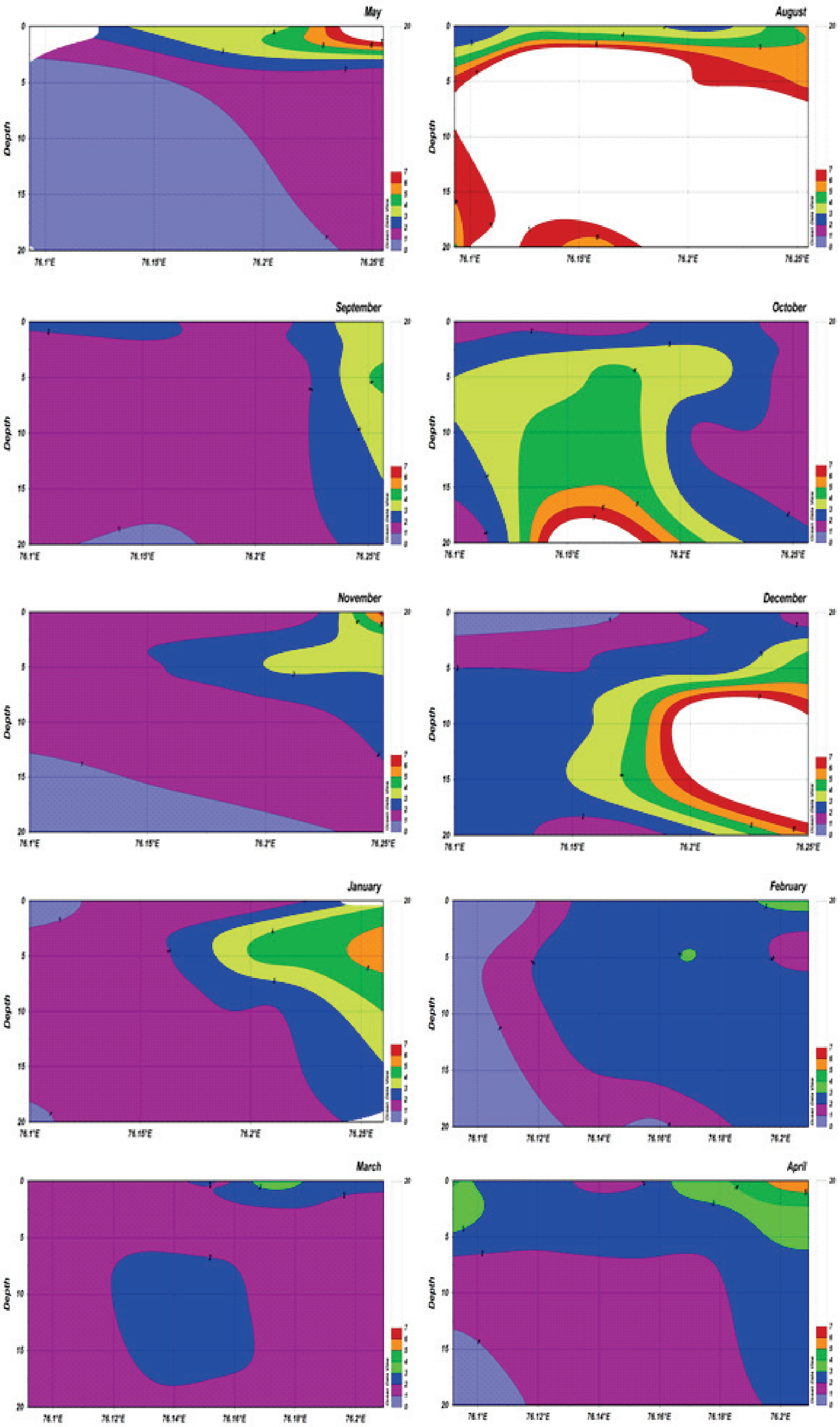

Fig. 2. Plots showing the Chlorophyll concentration of total phytoplankton from May 2013 to April 2014. X axis represents longitude and Y axis represents depth. Z axis represents the chlorophyll concentration

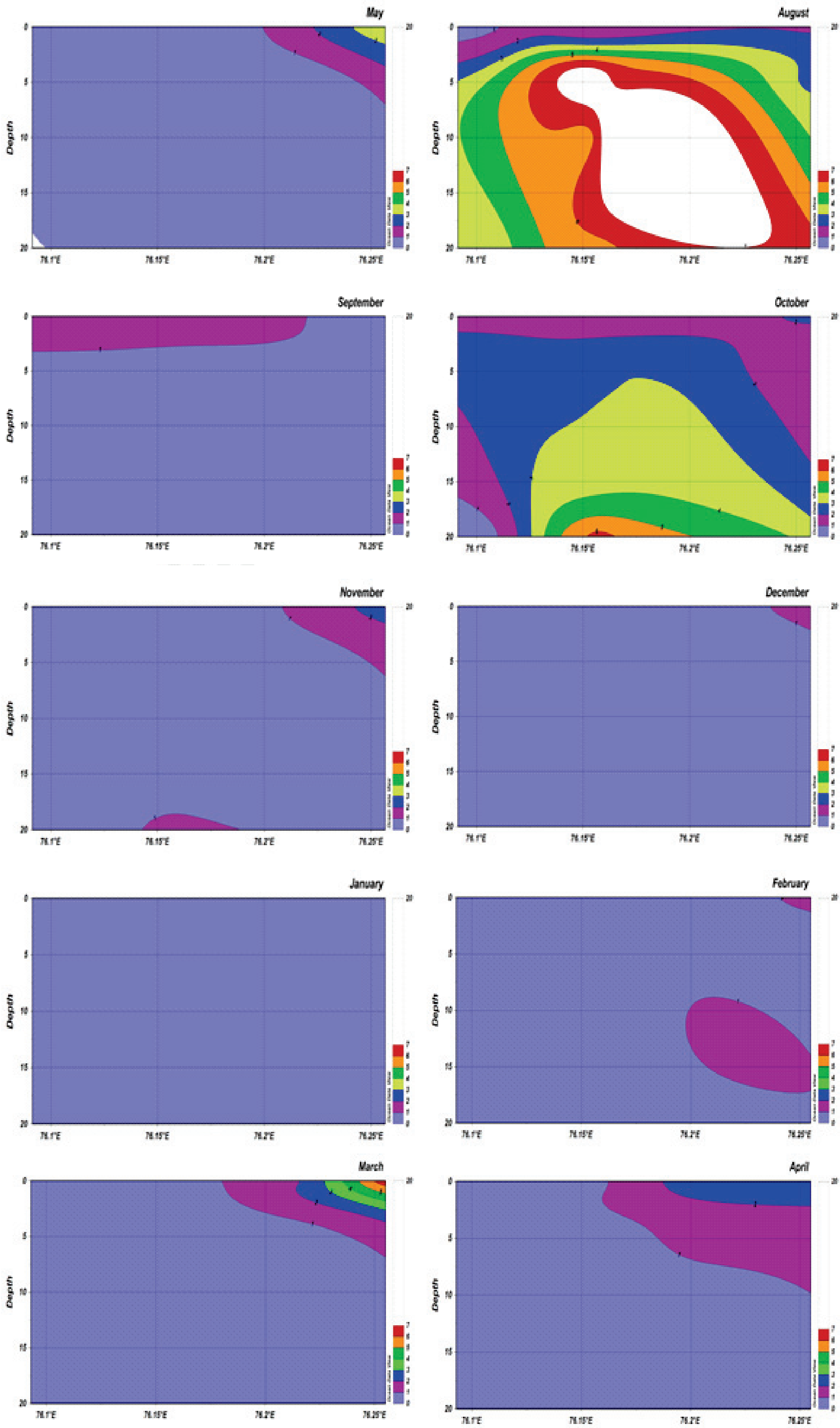

Fig. 3. Plots showing the Chlorophyll concentration of microphytoplankton from May 2013 to April 2014. X axis represents longitude and Y axis represents depth. Z axis represents the chlorophyll concentration

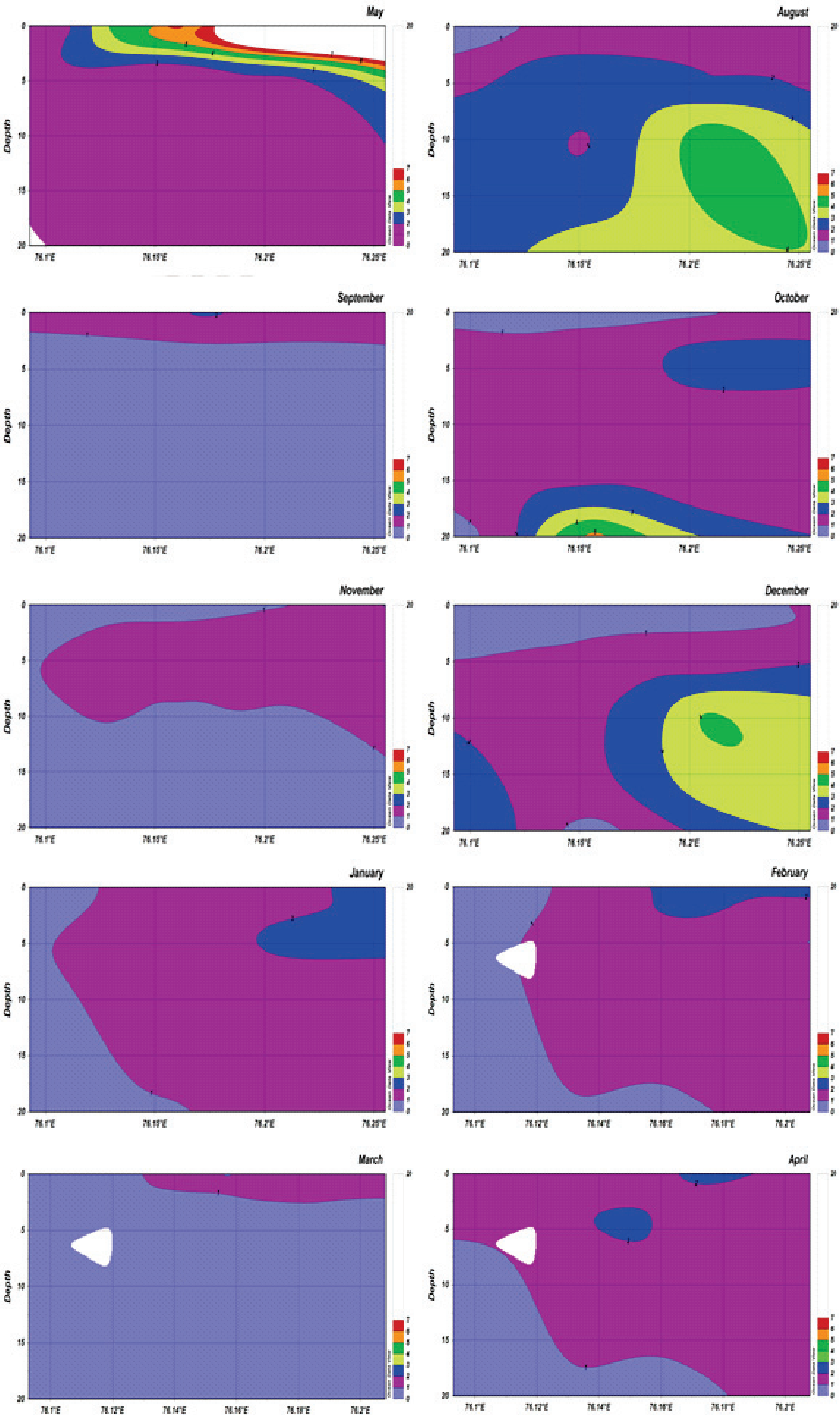

Fig. 4. Plots showing the Chlorophyll concentration of nanophytoplankton from May 2013 to April 2014. X axis represents longitude and Y axis represents depth. Z axis represents the chlorophyll concentration

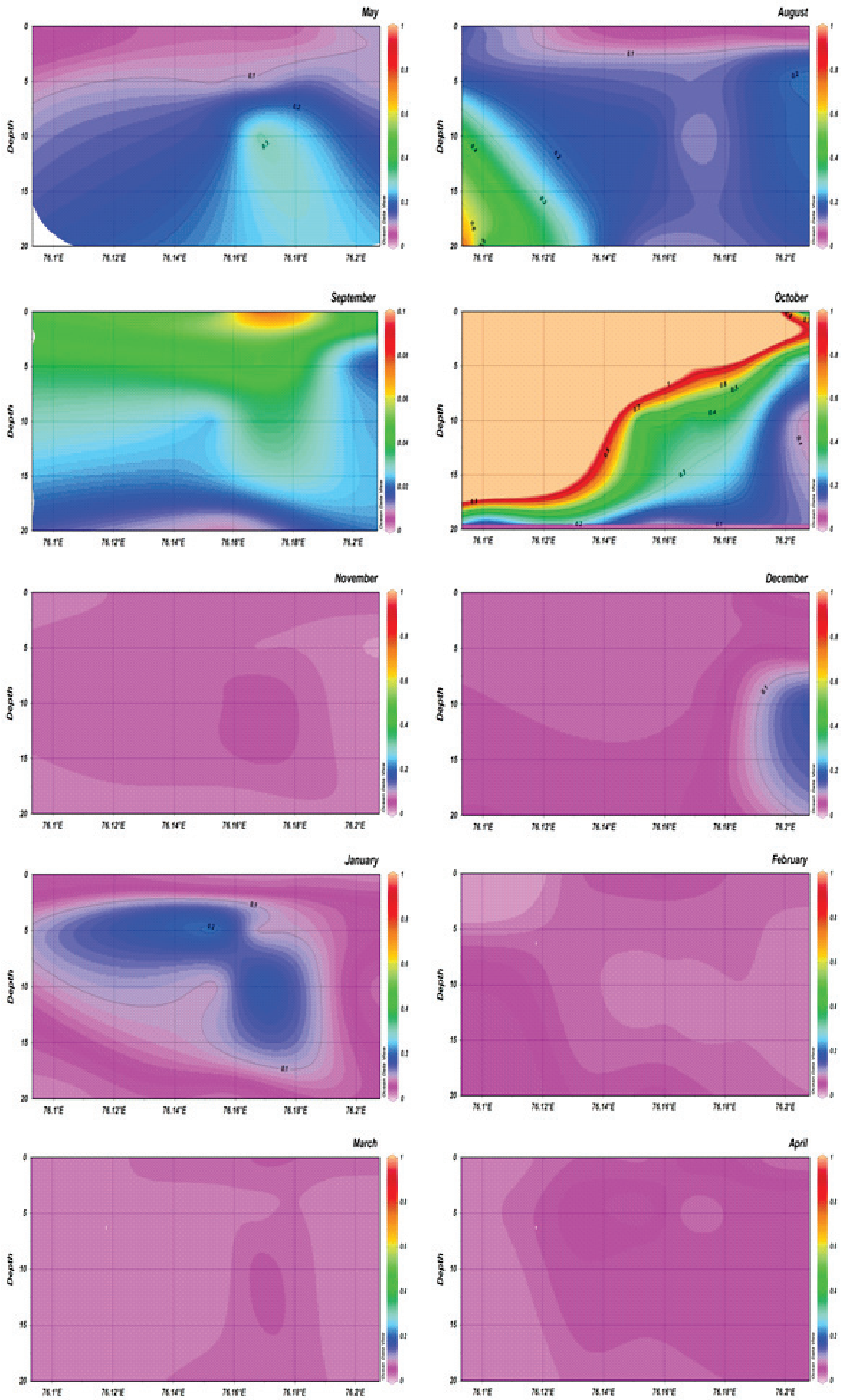

Fig. 5. Plots showing the Chlorophyll concentration of picophytoplankton from May 2013 to April 2014. X axis represents longitude and Y axis represents depth. Z axis represents the chlorophyll concentration

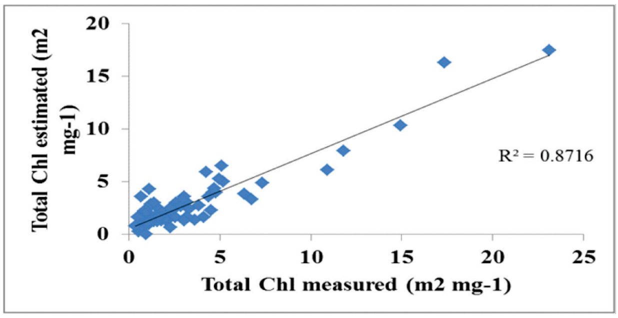

Fig. 6. Regression plot showing the relation between Total chlorophyll a measured and total chlorophyll estimated (sum of chlorophyll concentration measured in different size fractions).

The concentration of physico-chemical parameters *viz.,* total suspended sediment (TSM), Turbidity, Salinity, pH and Dissolved Oxygen (DO) was shown in Table 2.

Suspended sediments showed minimum variation horizontally and vertically in most of the months. During November, horizontal variation was detected in the 2-10m depth water column in the estuarine station was in the range of 0-10 mg L^{-1}.

Turbidity ranged from 0.19-19.1 NTU during the study period. The month of May had turbidity between 5-10 NTU except for 5-10m depth towards estuary, where the values ranged between 10-15 NTU. During August, neither vertical nor horizontal variability of turbidity was measured and in December, turbidity was high in the bottom waters of some stations and it extended upwards 5m depth. During January, turbid waters in the range 5-10NTU extended towards 5m depth of estuary while the surface waters showed minimum turbidity.

Salinity ranged from 34.50-36.45 psu with an average of 32.05±1.89. Salinity was high during May (34-36psu) in the surface and bottom waters of coastal stations. During May low saline waters was observed in the surface and 5m depth in the estuarine station. Monsoon season showed (August, September and October) similar salinity patterns to that during May. High vertical variability was observed in all stations. The salinity gradient was from 10 to 36 psu during these months.

pH varied from 7.3-8.4 during the study period. During May 2013, pH was between 8-8.25 in the surface waters and 5m depth of coastal stations.

Table 1. Table showing the minimum and maximum values of nutrients at surface, 5m, 10m and 20m depth during the study period

(μmol L^{-1})	0m	5m	10m	20m
Nitrite	0.02-3.58	0.02-3.87	0.11-4.69	0.03-4.08
Nitrate	0.29-30.59	0.59-20.70	1.58-16.93	4.86-30.59
Ammonia	0.06-14.42	0.14-10.06	0.10-6.48	1.03-6.1
Phosphate	0.38-3.11	0.57-2.17	0.43-2.25	1.09-2.87
Silicate	0.01-20.29	0.44-19.59	4.48-14.81	2.44-20.35

Table 2. Table showing the minimum and maximum values of physico-chemical parameters at surface, 5m, 10m and 20m depth during the study period

	0m	5m	10m	20m
TSM (mg L^{-1})	1.28-18.55	1.30-50.90	1.30-44.30	1.35-34.64
Turbidity (NTU)	0.51-13.80	0.80-43.50	2.50-20.50	0.19-19.50
Salinity (psu)	3.45-35.65	21.94-36.21	31.49-36.45	34.07-36.10
pH	7.33-8.37	7.44-8.19	7.51-7.94	7.52-8.01
DO (ml L^{-1})	2.01-6.01			

During August, the surface waters showed high alkalinity in the coastal waters. During September, the surface waters of estuarine station showed pH between 7.25 and 7.5 and in October, surface waters of coastal station changed to alkaline.

DO concentration ranged from 1.985 mg L^{-1} to 4.598 mg L^{-1}. In May, minimum DO of 1.985 mgL^{-1} and maximum of 4.5983 mg L^{-1} was measured at stations S4 and S1 respectively. During August, minimum and maximum DO was 4.01 mg L^{-1} and 6.01 mg L^{-1} at stations S6, S7 and S5 respectively. In September, the concentration ranged from 2.006-4.413 mgL^{-1}.

High Chl_{total} towards the estuarine side can be attributed to the mixing of seawater and river water. Chl_{micro} was high during August and October. It is due to the coastal upwelling experienced in this region of South-eastern Arabian Sea during monsoon (August) and spring inter-monsoon (October) for which conditions are characterized by weaker winds (wind speed 3.7 $msec^{-1}$) and higher SSTs (28ºC) bringing high nitrate bottom water to the surface off kochi region (Habeebrehman, 2008). Moreover, the depth of the 25ºC isotherm layer is reported as 5m in this area. (Lathika et al., 2016). High silicate and nitrate favours the microphytoplankton production in which diatoms are the major groups. Diatoms use silicate to make their siliceous frustules (Tett et al., 2003; Escaravage & Prins 2002; Kang et al., 2015; Krause et al., 2015). Increased ammonium concentration in the surface waters of this region during October facilitated the proliferation of dinoflagellates, since they have capacity to assimilate ammonia-N directly (Pernice et al., 2012). Microphytoplankton often represents larger fractions of Chl biomass in coastal areas and is responsible for new primary production (Forget et al., 2010). Chl_{nano} was high during May 2013. During May, phosphate, nitrite, ammonium and silicate concentration was low but nitrate was high. High nitrate and intermediate phosphate concentration favours growth of nanophytoplankton (Tilstone et al., 1999; Fang et al., 2006; Barnes et al., 2015). High concentration of Chl_{pico}during October along with high ammonium in surface water infers the presence of autotrophic Synechococcus. Synechococcus is the most abundant picoplankton in the upper, nutrient-rich layers of either upwelling or frontal systems of tropical and subtropical environments. (Linacre et al., 2015; Rajaneesh et al., 2015). Picophytoplanktons are characteristics of oligotrophic and dim light regions. High concentration of Chl_{pico} during October can be attributed to the increased concentration of ammonium and low concentration of silicate and nitrite (Mouriño-Carballido et al., 2016). Williams et al. (2002) has reported that total ammonium intake was higher in picoplankton when compared to nitrate. High ammonium concentration has favoured picophytoplankton growth. Eventhough high chlorophyll concentration was observed in the month of August, numerical density of phytoplankton were high during September. Picophytoplankton increment during pre-monsoon was due to coastal floods since the flood waters carry ammonia to the coastal waters (Rajaneesh et al., 2015; Prakash & Sheela, 2016). Phytoplankton community structure showed a clear variation from a dominant diatom to dinoflagellate and cyanophyte community (monsoon-post monsoon and pre-monsoon seasons) as evident from the microscopic cell counts (Minu et al., 2014). High chlorophyll, absorption by phytoplankton and numerical density are related with the pre showers and extended south west monsoon that prevailed in the region and associated river runoff trough estuary. It was also observed that microphytoplankton contribute more towards 10m depth, nanophytoplankton in the surface to 5m depth and picophytoplankton more in 10-20m water column.

The spatial and temporal variability in size fractionated chlorophyll *a* (Chl a) of Cochin coastal waters for the year 2013-14 was studied. From this study it can be concluded that southwest monsoon played an important role in determining the dominant size fraction of phytoplankton. But the consistency of the dominance has to be clearly understood. This study revealed the influence of chemicals on size classes of phytoplankton. Silicate, nitrate and ammonium favours the microphytoplnkton and high nitrate and intermediate phosphate enhance the nanoplankton while ammonia alone boost picophytoplankton. These data will provide an insight into the chemical factors that control the production cycle in this neritic system.

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