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Relationships Between the Hydrochemical Characteristics, Phytoplankton Chlorophyll and Phaeophytin in the Southwest Coast of India

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The relationship between the hydrochemical characteristics and phytoplankton chlorophyll in coastal pollution monitoring surveys, establishes a basis for understanding the trophic state of coastal waters in accordance with nutrient enrichment routing to progress in capture fishery. On the other hand, the zooplankton (including ichthyoplankton) grazing and its abundance can be understood from the quantification of detrital chlorophyll/phaeophytin. A collection of datasets for three years seasonal sampling (January 2008 to 2011) along Cochin and Mangalore (Southwest coast of India) was analyzed to find out the relationship between hydrochemical factors, chlorophyll *a* and phaeophytin contents. Principal component analysis (PCA) was used to analyze these ecological parameters interrelationship. In both the sampling sites, the nutrient factors statistically predict that nitrite is influenced by the concentration of chlorophyll *a* and its significant positive correlation to phaeophytin indicates the strength of micro zooplankton grazing. We infer that micro zooplankton grazing is an important factor in keeping a balanced coastal ecosystem at Cochin and Mangalore. The nutrient factors are totally utilized by the phytoplankton community. The PCA study confirms about assimilation of the dissolved inorganic nitrogen (DIN) in the form of NH_4^+ formed by the zooplankton excreta (detrital chlorophyll/phaeophytin) in Mangalore coastal waters.

Key words: *Chlorophyll, Phaeophytin, trophic state, hydrochemical characteristics, Arabian Sea*

Introduction

Variation in environmental factors caused by atmospheric forcing has led to fundamental differences in the pelagic marine ecosystem in terms of production[1-2]. The west coast of India (Arabian Sea) is a region of intense upwelling associated with southwest monsoon (May to September) whereas the east coast experiences only a weak upwelling associated with the northeast monsoon (October to January), resulting in marked differences in hydrographic regimes, productivity patterns and qualitative and quantitative composition of fisheries[3]. Productivity reasons explicated by the researchers concentrated in this region include the inflow of a network of rivers, backwaters, rocky shores and the intense upwelling associated with southwest monsoon influenced upon the improved nutrient composition[4]. Naturally occurring seasonal nutrient enrichment in the waters along the west coast resulted by the upwelling during the southwest monsoon period trigger high primary production and the stock of phytoplankton in terms of Chlorophyll *a*[5].

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The aim of this study was to describe the relationship of phytoplankton pigments and its detrital form with hydrological and nutrient concentrations using statistical tools such as hierarchical clustering and principal component analysis (PCA) in order to link the chemical analysis with the biology of the southwest coast of India, which is of importance for future management decisions.

Materials and methods

Sampling locations

Water sampling, *in situ* analysis and filtration process for chlorophyll *a* estimation were conducted onboard during the cruises of CRV *Sagar Purvi*, *Sagar Paschimi* (owned by the National Institute of Ocean Technology, India), purse seiner of Cochin and Mangalore from January 2008 to January 2011 at different seasons. Transects along Cochin (09°58'16"N; 76°14'43"E) and Mangalore (12°50'49"N; 74°49'17"E) were located from bar mouth towards sea at a distance of 0.5 km (Fig. 1). Samples were collected from these predetermined transects along Cochin and Mangalore. Coastal waters of Cochin and Mangalore were subjected to discharge

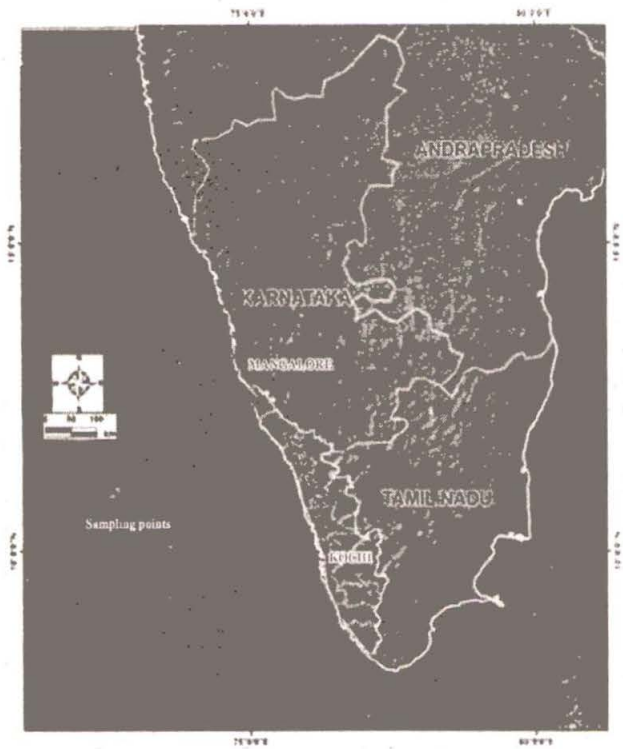

Fig. 1: The sampling locations at Cochin and Mangalore

of effluents from various major and minor industries situated on the riverbanks, fish landing centres and harbor operations. Cochin backwaters form a complex micro tidal estuary receiving 2 x 10^{10} m^3y^{-1} of fresh water through six rivers and join the southern west coast of India[6]. Mangalore bar mouth receives water from two rivers viz. Gurupur and Netravati. A major industrial town, Kulai situated north to the sampling site and on the banks of Gurupur River daily discharges the industrial waste to the river and finally reaching the coastal zone at Mangalore bar mouth[7].

Sampling protocol

Surface chlorophyll *a* concentrations were determined using Whatman 47 mm Ø GF/C fiber (0.7 µm nominal pore size). The contents were extracted in 90% acetone, centrifuged, refrigerated in dark for 20 to 24 hrs and the light absorbance at 750, 664, 647 and 630 nm was recorded in a spectrophotometer (Shimadzu UV 1800)[8]. Phaeophytin or chlorophyll degradation was determined by adding two drops of dilute hydrochloric acid to the cuvette and mixing thoroughly and re-measuring the extinction at 665 and 750 nm. Hydrographical parameters such as salinity (psu), pH and surface water temperature (SWT) in °C were measured *in situ* using probes (WTW Multi Line P4). Values of suspended sediment concentration (SSC) were determined as the weight of material retained on a GF/F membrane per volume unit after drying the filter for 2 h at 120°C. The chemical estimation of dissolved oxygen was done onboard by the modified Winkler's method. Nitrate-N (NO_3), Nitrite-N (NO_2), Ammonia (NH_4^+), Inorganic Phosphate (PO_4-P), Inorganic silicate (SiO_4-Si) in filtered samples and Total Nitrogen, Total Phosphorus in unfiltered samples were analyzed spectrophotometrically[9].

Statistical analysis

Hierarchical cluster analysis was used to investigate the statistical significance between stations based on the relationship of hydrological parameters to chlorophyll *a* and phaeophytin pigment concentration. The proximity measurement used is the Euclidean distance (the square root of the sum of the differences between the variables squared)[10]. Further, the data were separately subjected to descriptive statistics methods, principal component analysis (PCA) in order to find out the major components influencing and their percentage of variance using SPSS 16 Version.

Results

The dendrogram showing single linkage clustering of samples from Cochin and Mangalore using relative distances and the sums of squares agglomeration[11] is presented in Fig. 2. The dendrogram plotted revealed two meaningful clusters at Cochin and Mangalore transects indicating the similarities between hydrological parameters, chlorophyll *a* and phaeophytin pigments. Environmental variables and phytoplankton pigment concentration showed the presence of two statistically significant clusters at Cochin and Mangalore transects with 80 to 90% similarity irrespective of seasons. Positive correlations were found between pH, dissolved oxygen and SSC; major nutrient factors and micro algal pigment concentration. Hence these were grouped under the most correlation expressing clusters of shorter Euclidian distance (Fig. 2 a, b).

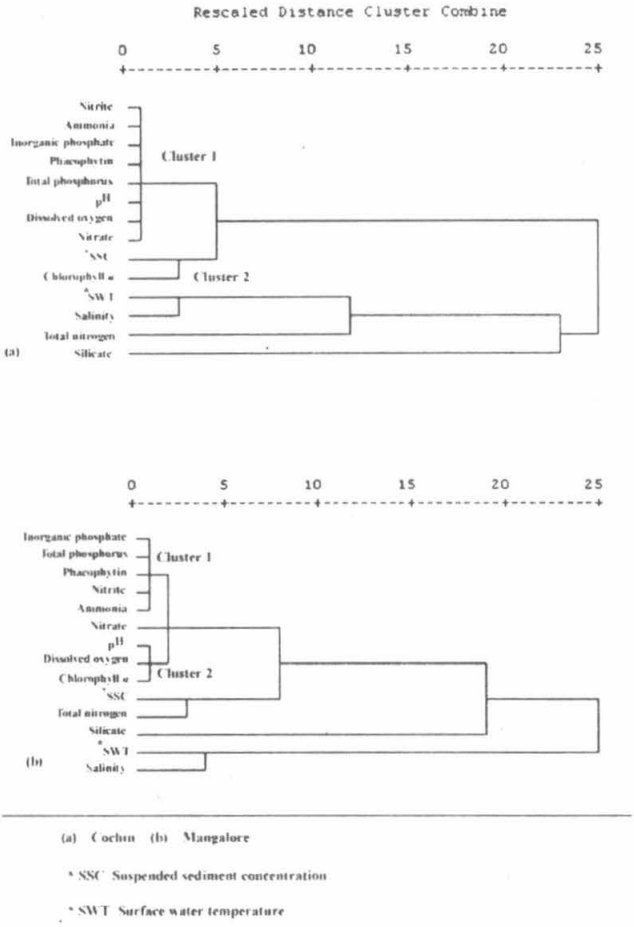

Fig. 2: Cluster analysis showing classification of hydrological parameters for sites Cochin and Mangalore

In order to preserve the robustness of this analysis, the number of chemical and biological characteristic in each study site was examined using principal component analysis (PCA) and the data is given in Table 1 and Table 2. In general, component matrix correlation coefficients greater than 0.6 could be taken for interpretation[12]. At Cochin, PCA extracted three components (hereafter referred to as PC1 to PC3) matrix (Table 1), which explains 73.7% of total variance and they may be directly linked with inflow of nutrients by river, productivity indicated through phytoplankton pigment concentration and zooplankton grazing assessed by phaeophytin concentration.

Table 1.: Component matrix extracted using PCA and their % contribution to explaining the variance in the whole dataset (combined = 73.7%) for environmental variables at Cochin

Component Matrix			
	Component		
	PC1	PC2	PC3
	38.7 %	18.2 %	16.8 %
SWT	-0.716	0.325	0.302
SSC	-0.693	0.255	-0.148
PH	-0.569	-0.653	-0.069
Salinity	-0.872	-0.255	-0.193
Dissolved oxygen	0.7	0.338	-0.434
Nitrite	0.157	-0.691	0.399
Nitrate	0.767	-0.206	0.032
Ammonia	0.586	-0.325	0.487
Total nitrogen	0.239	0.508	-0.029
Inorganic phosphate	0.922	-0.099	0.094
Total phosphorus	0.925	0.046	0.025
Silicate	0.885	0.155	0.226
Chlorophyll *a*	-0.255	0.656	0.622
Phaeophytin	-0.357	0.015	0.856

The individual PCA coefficients are presented in Table 1. PC1 explains 44.7% of the total variance and can be used to distinguish samples located within the extraction areas. In this component, the most notable observation was that the dissolved oxygen, nitrate, PO_4-P, Total Phosphorus and SiO_4-Si exhibited negative correlation to SWT, SSC and salinity. Negative values could be due to the mixing and dilution of coastal waters during water exchange from freshwater bodies whereas positive values of PC1 indicated nutrient inflow to coastal waters. PC2 explains 15.18% of the total variance and could be interpreted to describe the primary productivity of

the surface water column. Positive values correspond to phytoplankton standing crop (total chlorophyll - chlorophyll *a*) while negative correlation to nitrite indicates daytime release of nitrite by phytoplankton. PC3 corresponds to strong positive correlation of chlorophyll *a* to phaeophytin that can be used to give detailed information about the grazing strength of zooplankton leading to secondary production and energy flow.

A cumulative 73.7% variance was observed in Mangalore as that of Cochin (Table 2). The PCA distinguished four components (hereafter referred to as PC4 to PC7) in the Mangalore transect (Table 2). Positive values of PC4 correspond to the input of industrial contaminants resulting in organic enrichment. In this principal component nitrate, PO_4-P, Total Phosphorus, SiO_4-Si showed negative correlation to pH and salinity. Negative values indicate the presence of industrial acidic pollutants. PC5 indicates upwelling and nitrite production routed by resting stage phytoplankton. PC6 values reflect the micro zooplankton grazing and the dominance of herbivore zooplankton. Positive values of PC7 indicate the presence of DIN in the form of ammonia contributed by riverine influx and increased concentration of phaeophytin in the form of zooplankton excreta.

Table 2.: Component matrix extracted using PCA and their % contribution to explaining the variance in the whole dataset (combined = 73.6%) for environmental variables at Mangalore

Component Matrix				
	Component			
	PC4	PC5	PC6	PC7
	31.2 %	21.1 %	13.8 %	7.5 %
SWT	-0.237	0.558	0.404	0.143
SSC	-0.062	**0.918**	-0.076	-0.027
PH	**-0.757**	0.157	-0.233	0
Salinity	**-0.882**	0.283	-0.071	0.063
Dissolved oxygen	0.107	0.58	0.279	0.01
Nitrite	0.077	**0.836**	0.015	0.048
Nitrate	**0.65**	0.581	0.041	-0.105
Ammonia	0.007	-0.118	0.037	**0.973**
Total nitrogen	0.469	0.352	-0.188	0.12
Inorganic phosphate	**0.895**	-0.042	0.165	0.092
Total phosphorus	**0.806**	-0.217	0.168	0.09
Silicate	**0.908**	-0.067	0.075	-0.124
Chlorophyll *a*	-0.458	-0.396	**0.697**	-0.085
Phaeophytin	-0.167	0.108	**0.894**	-0.033

During the three year period investigated (January 2008 to January 2011), total chlorophyll *a* concentrations were highly variable across the study region and fell in the range of 2.14 to 22.75 mg m^{-3} with a mean of 10.28 mg m^{-3} in Cochin and 1.33 to 13.14 mg m^{-3} with a mean of 5.68 mg m^{-3} in Mangalore. The mean phaeophytin concentrations at Cochin and Mangalore were 2.21 and 1.63 mg m^{-3} respectively. However, the influence and relationship of hydrological parameters to phytoplankton pigment and phaeophytin at Cochin and Mangalore coastal waters showed good homogeneity among the situations examined.

Discussion

One of the major findings from this study is that the riverine fresh water fluxes interact closely with coastal marine waters through tide movement and mixing. This study has also evidenced that large input of nutrients into the coastal waters of Cochin and Mangalore irrespective of seasons, mainly originating from domestic sewage and industrial effluents[7-13]. In terms of pigment contents and their concentrations, a negative correlation of nitrite to total chlorophyll in PCA in Cochin indicated daytime release of nitrite by phytoplankton and its rapid conversion to other nitrogen forms by nitrifiers/ denitrifiers present in the water column. The Arabian Sea is considered as one of the three major open ocean denitrification zones in the world and the coastal versus open ocean denitrification was well documented[14]. Phytoplankton biomass estimates by counting and volume assessment of cells, and measurement of pigment concentration, are widely used to estimate algal biomass is of major concern in aquatic ecological studies[15]. Chlorophyll *a* is common to all photosynthetic organisms and its concentration is used extensively for estimating phytoplankton biomass.

The statistical technique, hierarchical clustering has the disadvantage that division may be imposed when they have little ecological meaning and it is sometimes difficult to decide what constitutes a group. Further, differences among groups cannot be directly tested. In order to find out the relationship between hydrological factors and pigment contents in surface water column of Cochin and Mangalore coast, the water samples analyzed and the data sets were separately focused to principal component analysis (PCA).

In the present study, a significant correlation between SSC which indicates turbidity and nitrite has been noted. As described earlier the Secchi depth at coastal Mangalore is approximately 0.5 m, due to high turbidity resulting from the upwelling most probably induced by southwest monsoon and subsequently benthic resting stages of diatom contribute by seeding the water column, they can influence the standing crop of phytoplankton community[16]. The significant positive correlation between total chlorophyll and phaeophytin pronounced throughout the three year study period of Cochin and Mangalore revealed the micro zooplankton grazing. The role of the micro zooplankton as phytoplankton consumers in the different marine habitats accounts for an average of 67% and 60 to 75% of daily phytoplankton production and growth respectively[17].

Unlike the nutrient distribution by pollutant inflow[18], total chlorophyll was high at Cochin indicating the eutrophic state and a well balanced ecosystem is maintained by zooplankton grazing. Maximum chlorophyll *a* recorded in the Cochin back water system was 47 mg m^{-3} [13]. The range of chlorophyll *a* values at Mangalore inferred that the trophic state is mesotrophic as the phytoplankton production is low due to turbid waters and maximal consumption by zooplankton. Positive correlation of DIN in the form of ammonia in a PCA extracted component at Mangalore can be a chance of detrital chlorophyll routed from the zooplankton excreta dissolved in coastal waters other than river inflow. Increased nitrogen loading from land to coastal waters through river runoff is the main way of DIN to Arabian Sea[14].

Conclusion

The results of this study lead to infer that micro zooplankton grazing is an important component in balancing the trophic state and averting the chances of harmful algal blooms (HABs) at Cochin and Mangalore transects. Cochin generally showed increased phytoplankton standing crop routed by enriched nutrient inflow with a concomitant increase in micro zooplankton grazing. On the contrary, at Mangalore, the productivity though enhanced by nutrient inflow, is hindered by high SSC that keeps the trophic state under slightly eutrophic condition. In addition, the vertical drift of resting stage diatom to favorable condition through up welled waters reinforced by micro zooplankton grazing strength was conspicuous.

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