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Research Article

Hydro Chemical Characteristics and Biological Response of the Cochin Coastal Waters-Southwest Coast of India

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Abstract

Hydrography and the associated chemical and biological responses of the Cochin coastal waters were studied during the monsoon, post-monsoon, and pre-monsoon periods. During monsoon, the surface waters were cold (SST = 27.2-27.8°C), of low salinity (salinity = 30.3-33.5 psu), and oxygen deficient (O_2 = 178-180 µmol/L), with a high enrichment of nutrients ($NO_3 \geq 4$ µmol/L, $PO_4 \geq 1.2$ µmol/L, and $SiO_4 \geq 6$ µmol/L), which indicates a hypertrophic environment (chlorophyll *a* ≥ 5 mg/m^3). During post-monsoon season, the surface waters were slightly warmer (SST = 28.6-29.2° C), of low salinity (salinity = 30.8-34.0 psu), and less oxygenated (O_2 = 185-189 µmol/L), with a moderate enrichment of nutrients ($NO_3 \geq 2$ µmol/L, $PO_4 \geq 1$ µmol/L, and $SiO_4 \geq 4$ µmol/L), which indicates a eutrophic environment (chlorophyll a = 4 - 5 mg/m^3). During pre-monsoon season, the surface waters were very warm (SST = 29.5-30.2° C), of low salinity (salinity = 31.3-34.3 psu), and the oxygen level was under saturated (O_2 = 190-196 µmol/L), with a slight enrichment of nutrients ($NO_3 \geq 1$ µmol/L, $PO_4 \geq 0.8$ µmol/L, and $SiO_4 \geq 2$ µmol/L), which indicates an oligotrophic environment (chlorophyll a ≤ 1 mg/m^3). The enhancement of chlorophyll a that was observed in the shelf waters off Cochin from the pre-monsoon to the post-monsoon seasons and from the post-monsoon to the monsoon seasons was caused by the increasing bioavailability of nutrients from anthropogenic sources on land that were discharged through the rivers.

Keywords: Chlorophyll a; Cochin coastal waters; Hydrochemistry; Hypoxia; Nutrient

Introduction

Human activities on land increase the loading of nutrients (nitrogen [N], phosphorous [P], and silicon [Si]) and organic matter above naturally found levels in rivers and estuaries, which has impacts on the biogeochemical cycling in coastal marine environments worldwide [1-4]. For instance, over the past few decades, anthropogenic pressures within the riverine catchments of the Vembanad Lake have dramatically increased the loading of organic matter above naturally found levels, which has accelerated eutrophication and provoked severe hypoxic events at the continental shelf waters off Cochin [5-6]. This increase in the supply of organic matter comes from external sources or from new production within the coastal system through biologically mediated processes stimulated by increased additions of nutrients from the land [7]. However, even though the coastal waters of India are being impacted by an enhanced nutrient loading through land runoff and atmospheric deposition, there are only a few studies that have investigated the effects of eutrophication and hypoxia on the biogeochemical cycling of carbon and nutrients such as nitrate, phosphate, and silicate [6,8-12]. Understanding the biogeochemical behavior of nutrients in coastal waters has important implications for estimating global nutrient fluxes and for controlling eutrophication events [3,13].

The fate and distribution of nutrients (N, P, and Si) in the coastal waters of India differ widely with space and time, and they are controlled by a variety of physical, chemical, and biological processes [6,14-17]. The anthropogenic sources that enhance nutrient concentrations in the coastal waters of India are from atmospheric deposition due to the burning of fossil fuels and by effluent discharges from industries, agricultural fields, aquaculture fields, and domestic sectors [18]. Consequently, apart from the nutrient fertilization that is transported via deep (approximately 50 to 75 m) upwellings of oceanic waters (a natural source), by means of wet and dry depositions from the anthropogenic sources on land, rivers also transports approximately 0.6 million tonnes of nitrogen and approximately 0.1 million tones of phosphorus annually to the coastal waters of India [6,7,19,20]. Hence, it is hypothesized that the continuous loading of nutrients (N and P) in surface waters from anthropogenic sources on land stimulates bio-availability and enhances eutrophication events. This is accomplished via rapid phytoplankton production (excess organic matter), which leads to the formation of algal blooms (for example, red tides). The subsequent oxidation in sub-surface or bottom waters results in an intensification and expansion of the naturally upwelled hypoxic zone over the western continental shelf of India [21,22]. The present study attempts to evaluate hydro chemical characteristics and their linkage with chlorophyll a concentrations along the shelf waters off Cochin.

Materials and Methods

Environmental Settings of the Study Area

Cochin, a densely populated (approximately 6,250 people per km^2) and industrialized city (approximately 250 types of chemical industries), is situated at the northern tip of the Vembanad Lake along the tropical belt of the southwest coast of India. The shelf waters off Cochin are subjected to marked continental influence due to the large volume of fresh water discharges (2.0 x 10^{10} m^3/yr) from the Periyar, Chalakudy, Muvattupuzha, Pampa, Manimala, Meenachil, and Achankovil rivers [23]. These rivers have their catchments in the Western Ghats, and they serve as the main inland freshwater resource for domestic, industrial, and irrigation purposes. Consequently, along with the freshwater runoff, these rivers also transport large volumes of municipal sewage (2,550 million liters per day [MLD]), industrial waste water (400 MLD), and organic waste (approximately 260 tonnes per day) from the Cochin city and agricultural effluents from the Kuttanad paddy fields into the Vembanad Lake [24]. The effluents discharged from the industrial, domestic, and agricultural areas of the Vembanad Lake riverine catchments are rich in nutrients and are gradually dispersed to the shelf waters off Cochin by tidal currents [25]. These anthropogenic inputs are expected to modify the biogeochemical cycling in the continental shelf waters off Cochin [6,24].

Sampling and Analytical Procedures

Hydrochemical measurements (that is, temperature, salinity, dissolved oxygen, nitrate-nitrogen, nitrite-nitrogen, phosphate-phosphorus, and silicate-silicon) and biological measurements (that is, chlorophyll a) were carried out in the Cochin coastal waters during the monsoon (July 2015), post-monsoon (December 2015), and pre-monsoon (March 2016) seasons. Five stations (1 to 5) with a bottom depth of 10, 12, 20, 30, and 50 m were selected at the mouth of the Cochin estuary for water sampling (Figure 1), with the goal of understanding the effects of anthropogenic terrestrial inputs on the water quality of this region [6]. The continental shelf in that area is classified into three regions, with stations 1 and 2 being near the shore, stations 3 and 4 were over the inner shelf, and station 5 was over the mid shelf. Water samples were collected using a 5 L Niskin sampler (Hydrobios-Kiel) from standard depths (the surface [1m depth] and the bottom), according to the Joint Global Ocean Flux Study *(*JGOFS) protocols [26]. The temperature was measured using a sensitive centigrade thermometer (accuracy ± 0.1˚C) with a graduation of 0-50˚C. The salinity was measured using a digital salinometer (DIGI-AUTO model 3G, Tsurumi Seiki, Japan; accuracy ± 0.001 psu) after calibration with standard sea water. Nutrients (nitrate-nitrogen, nitrite-nitrogen, phosphate-phosphorus, and silicate-silicon) were analyzed by following the standard colorimetric techniques using a SKALAR Segmented Flow Auto Analyzer (Model SA-1050) [27]. Dissolved oxygen was estimated by the Winkler's method of titration [27]. The analytical precision of the nutrient measurement was ± 0.10 µmol N/L for nitrate, ± 0.02 µmol N/L for nitrite, ± 0.04 µmol P/L for phosphate, and ± 0.05 µmol Si/L for silicate. Water samples (2 L) for chlorophyll a measurements were filtered through What man 47 mm GF/F filter (nominal pore size 0.7 µm) under gentle vacuum (< 50 mm Hg pressure) and stored at -20˚C until the analysis. Chlorophyll *a* in the filters was extracted with 10ml 90% acetone at 4˚C in the dark for 12 hours [28], and it was estimated spectrophotometrically (Perkin-Elmer, UV/Vis).

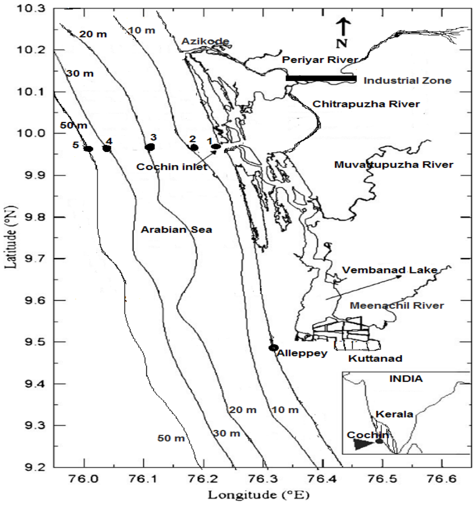

Figure 1: Map of the Cochin coastal waters with station locations.

Results

Hydrographical Features

The hydrographical parameters (that is, temperature, salinity, and dissolved oxygen), measured during the monsoon, post-monsoon, and pre-monsoon seasons are shown in (Figures 2 to 7).

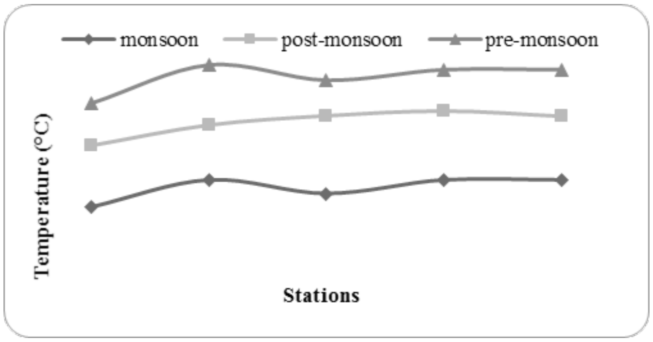

Figure 2: Distribution of temperature (˚C) at surface waters.

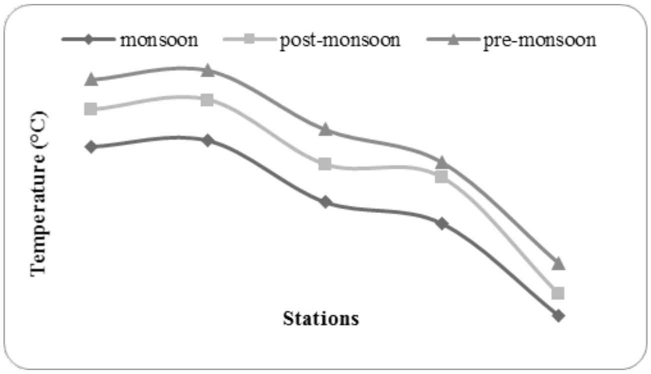

Figure 3: Distribution of temperature (˚C) at bottom waters.

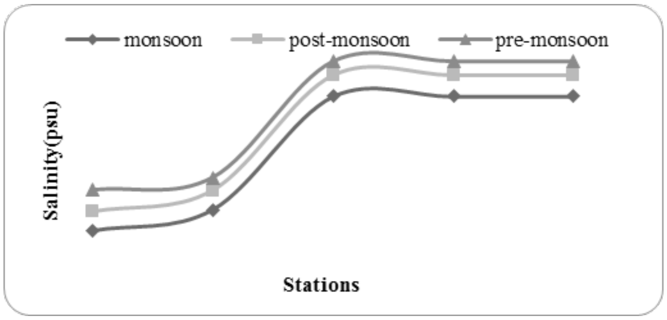

Figure 4: Distribution of salinity (psu) at surface waters.

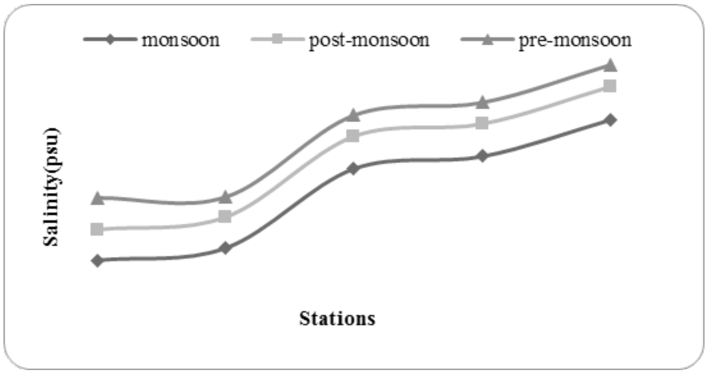

Figure 5: Distribution of salinity (psu) at bottom waters.

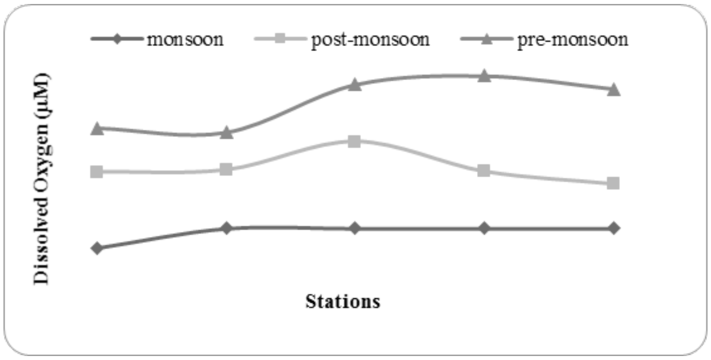

Figure 6: Distribution of dissolved oxygen (µmol/l) at surface waters.

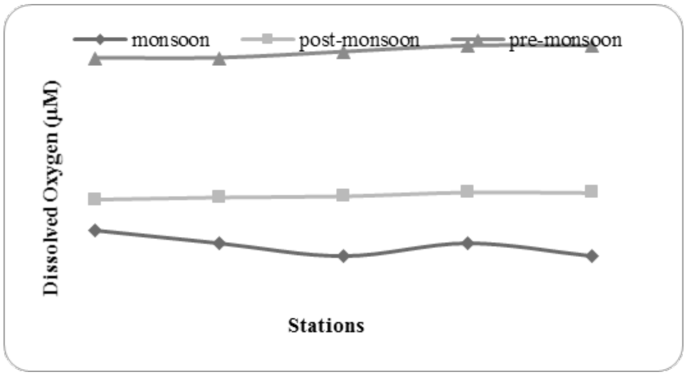

Figure 7: Distribution of dissolved oxygen (µmol/l) at bottom waters.

Temperature

Sea Surface Temperature (SST) ranged from 27.2 to 27.8˚C, 28.6 to 29.2˚C, and 29.5 to 30.2˚C (Figure 2) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively.

The average SST values for the monsoon, post-monsoon, and pre-monsoon periods were 27.6 ± 0.3˚C, 29.1 ± 0.3˚C and 30.0 ± 0.3˚C, respectively. Similarly, the bottom temperature values ranged from 20.8 to 26.5˚C, 21.5 to 27.8˚C, and 22.5 to 28.8˚C (Figure 3**)** during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average bottom temperature values for the monsoon, post-monsoon, and pre-monsoon periods were 24.4 ± 2.3˚C, 25.6 ± 2.5˚C, and 26.5 ± 2.5˚C, respectively. The average SST values during the monsoon and post-monsoon periods were 2.4˚C and 1.5˚C lower, respectively, than the pre-monsoon period. Similarly, the average bottom temperatures during the monsoon and post-monsoon periods were 2.1˚C and 0.9˚C lower, respectively, than the pre-monsoon period.

Salinity

Sea Surface Salinity (SSS) ranged from 30.3 to 33.5 psu, 30.8 to 34.0 psu, and 31.3 to 34.3 psu (Figure 4) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average SSS values during the monsoon, post-monsoon, and pre-monsoon periods were 32.3 ± 1.6 psu, 32.8 ± 1.6 psu, and 33.2 ± 1.6 psu, respectively. Similarly, bottom salinity values ranged from 33.3 to 35.6 psu, 33.8 to 36.1 psu, and 34.3 to 36.5 psu (Figure 5), during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average bottom salinity values for the monsoon, post-monsoon, and pre-monsoon periods were 34.4 ± 1.0 psu, 35.0 ± 1.0 psu, and 35.3 ± 1.0 psu, respectively. The average surface and bottom salinity values during the monsoon and post-monsoon periods were 0.9 psu and 0.4 psu lower, respectively, than the pre-monsoon period.

Dissolved Oxygen

Dissolved oxygen concentrations in surface waters ranged from 178 to 180 µmol/L, 185 to 189 µmol/L, and 190 to 196 µmol/L (Figure 6) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average dissolved oxygen content in surface waters during the monsoon, post-monsoon, and pre-monsoon periods were 180 ± 0.9 µmol/L, 186 ± 0.6 µmol/L, and 193 ± 2.7 µmol/L, respectively. Similarly, dissolved oxygen concentrations in bottom waters ranged from 14 to 18 µmol/L, 23 to 24 µmol/L, and 46 to 48 µmol/L (Figure 7) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average dissolved oxygen content in bottom waters during the monsoon, post-monsoon, and pre-monsoon periods were 16 ± 1.7 µmol/L, 24 ± 0.6 µmol/L, and 47 ± 1.0 µmol/L, respectively. Similar to monsoon and post-monsoon periods, the bottom waters were also very low oxygenated during the pre-monsoon period.

Nutrients

The nutrient concentrations (nitrate, nitrite, phosphate, and silicate) measured during the monsoon, post-monsoon, and pre-monsoon periods are shown in Figures 8 to 15.

Nitrate concentrations in surface waters varied from 5.88 to 8.58 µmol/L, 2.35 to 3.05 µmol/L, and 0.88 to 1.28 µmol/L (Figure 8), during the monsoon, post-monsoon and pre-monsoon periods. The average nitrate content in surface waters during the monsoon, post-monsoon, and pre-monsoon periods were 7.42 ± 1.18 µmol/L, 2.73 ± 0.28 µmol/L, and 1.11 ± 0.17 µmol/L, respectively. Similarly, nitrate concentrations in bottom waters varied from 10.25 to 20.65 µmol/L, 3.55 to 7.28 µmol/L, and 1.55 to 3.15 µmol/L (Figure 9) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average nitrate content in bottom waters during the monsoon, post-monsoon, and pre-monsoon periods were 13.73 ± 4.79 µmol/L, 4.84 ± 1.69 µmol/L, and 2.07 ± 0.73 µmol/L, respectively. The average nitrate content in surface and bottom waters during the monsoon and post-monsoon seasons were approximately 6.6 and 2.4 times higher, respectively, than during the pre-monsoon season.

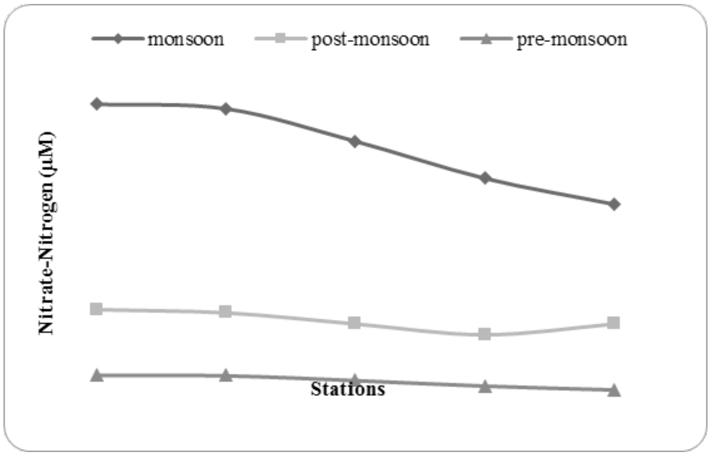

Figure 8: Distribution of nitrate (µmol/l) at surface waters.

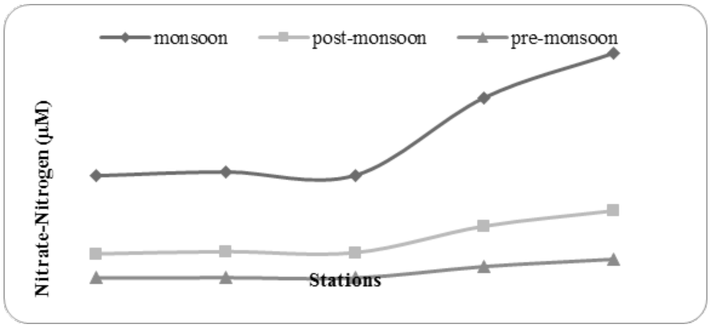

Figure 9: Distribution of nitrate (µmol/l) at bottom waters.

Nitrite concentrations in surface waters varied from 0.45 to 0.58 µmol/L, 0.38 to 0.49 µmol/L, and 0.29 to 0.38 µmol/L (Figure 10) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average nitrite content in surface waters during the monsoon, post-monsoon, and pre-monsoon periods were 0.48 ± 0.06 µmol/L, 0.41 ± 0.05 µmol/L, and 0.31 ± 0.04 µmol/L, respectively. Similarly, nitrite concentrations in bottom waters varied from 2.58 to 2.95 µmol/L, 2.18 to 2.51 µmol/L, and 1.68 to 1.95 µmol/L (Figure 11) during the monsoon, post-monsoon, and pre-monsoon seasons. The average nitrite content in bottom waters during the monsoon, post-monsoon, and pre-monsoon seasons were 2.80 ± 0.14 µmol/L, 2.39 ± 0.13 µmol/L, and 1.83 ± 0.10 µmol/L, respectively. The average nitrite content in surface and bottom waters during the monsoon and post-monsoon seasons were approximately 1.5 and 1.3 times higher, respectively, than that of the pre-monsoon season.

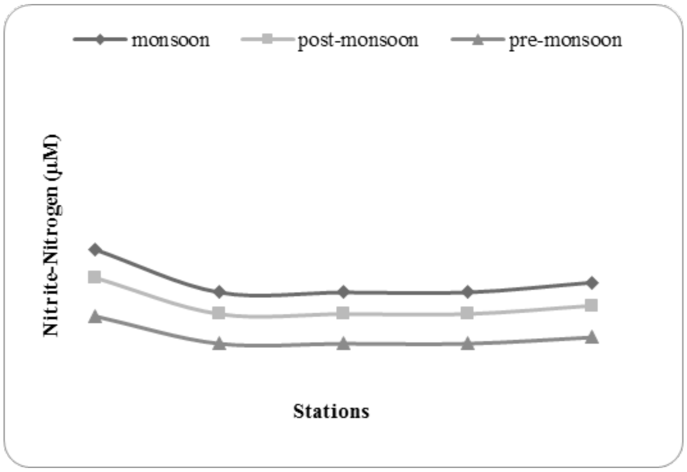

Figure 10: Distribution of nitrite (µmol/l) at surface waters.

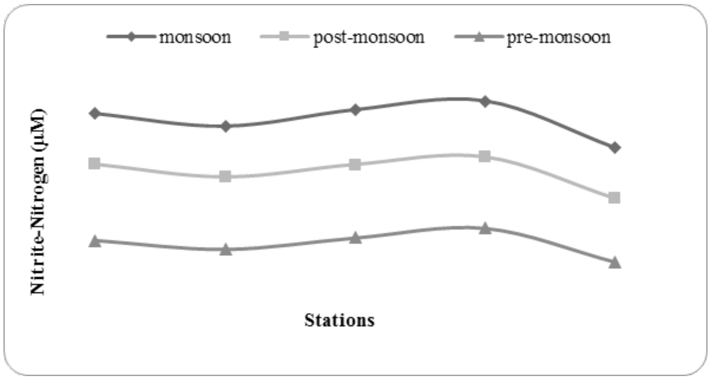

Figure 11: Distribution of nitrite (µmol/l) at bottom waters.

Phosphate concentrations in surface waters varied from 0.98 to 1.25 µmol/L, 0.85 to 1.06 µmol/L, and 0.64 to 0.81 µmol/L (Figure 12) during the monsoon, post-monsoon, and pre-monsoon seasons. The average phosphate content in surface waters during the monsoon, post-monsoon, and pre-monsoon periods were 1.16 ± 0.11 µmol/L, 1.01 ± 0.09 µmol/L, and 0.76 ± 0.07 µmol/L, respectively. Similarly, phosphate concentrations in bottom waters varied from 1.56 to 2.46 µmol/L, 1.33 to 2.09 µmol/L, and 1.01 to 1.60 µmol/L (Figure 13) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average phosphate content in bottom waters during the monsoon, post-monsoon, and pre-monsoon periods were 1.90 ± 0.40 µmol/L, 1.62 ± 0.34 µmol/L, and 1.24 ± 0.26 µmol/L, respectively. The average phosphate content in surface and bottom waters during the monsoon and post-monsoon periods were approximately 1.5 and 1.3 times higher, respectively, than that of the pre-monsoon period.

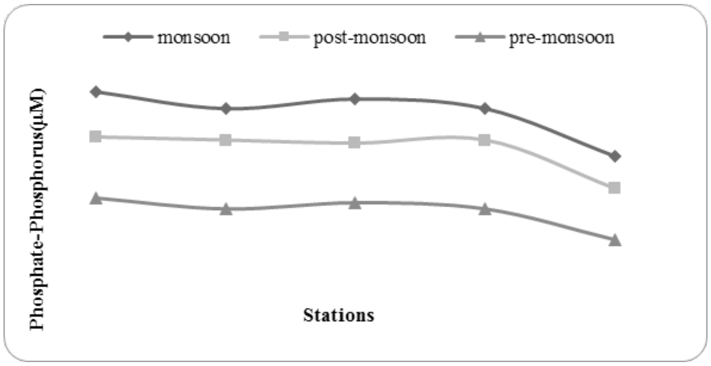

Figure 12: Distribution of phosphate (µmol/l) at surface waters.

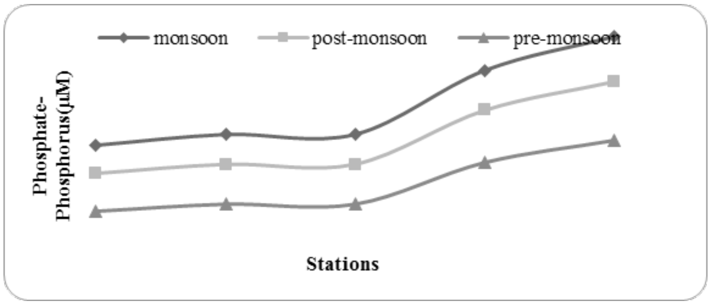

Figure 13: Distribution of phosphate (µmol/l) at bottom waters.

Silicate concentrations in surface waters varied from 5.33 to 6.85 µmol/L, 4.08 to 5.15 µmol/L, and 3.65 to 4.68 µmol/L (Figure 14) during the monsoon, post-monsoon, and pre-monsoon periods, respectively. The average silicate content in surface waters during the monsoon, post-monsoon, and pre-monsoon seasons were 6.21 ± 0.58 µmol/L, 4.58 ± 0.39 µmol/L, and 4.22 ± 0.37 µmol/L, respectively. Similarly, silicate concentrations in bottom waters varied from 7.45 to 21.46 µmol/L, 5.58 to 16.35 µmol/L, and 5.07 to 14.65 µmol/L (Figure 15) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average silicate content in bottom waters during the monsoon, post-monsoon, and pre-monsoon seasons were 12.76 ± 6.71 µmol/L, 9.62 ± 5.10 µmol/L, and 8.68 ± 4.57 µmol/L, respectively. The average silicate content in surface and bottom waters during the monsoon and post-monsoon seasons were approximately 1.5 and 1.1 times higher, respectively, than that of the pre-monsoon season.

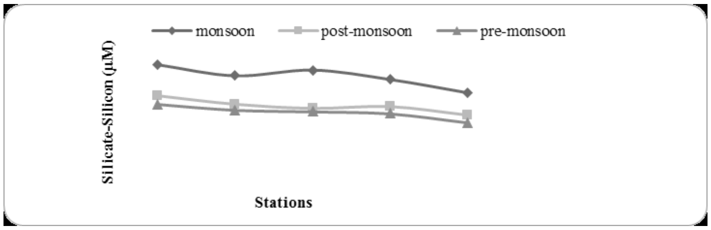

Figure 14: Distribution of silicate (µmol/l) at surface waters.

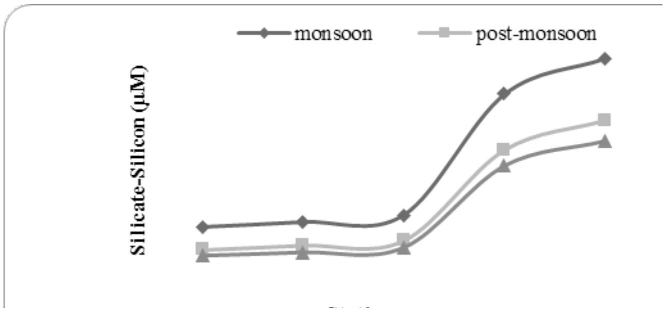

Figure 15: Distribution of silicate (µmol/l) at bottom waters.

Nutrient Stoichiometry

The molar ratio of nitrate to phosphate (N/P = 16) represents the Redfield ratio, and it is used as an indicator for finding which nutrient limits primary productivity in a given body of water [29,30]. Nitrogen acts as a limiting nutrient for primary productivity if the N/P ratio is less than 16, whereas phosphorus acts as a limiting nutrient for primary productivity if the N/P ratio is greater than 16. N/P ratios in surface waters ranged from 5.58 to 7.17, 1.99 to 2.70, and 1.29 to 1.65 (Figure 16) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. Similarly, N/P ratios in bottom waters ranged from 6.23 to 8.39, 2.22 to 2.96, and 1.45 to 1.97 (Figure 17) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. N/P ratios of surface waters were found to be lower than that of bottom waters. N/P ratios of surface and bottom waters were all well below the Redfield ratio of 16, suggesting that nitrogen acts as the limiting nutrient for primary production in the shelf waters off Cochin. Low N/P ratios further indicate intense denitrification activity in the shelf waters off Cochin [10].

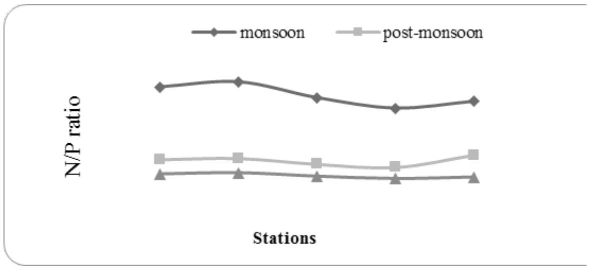

Figure 16: Distribution of N/P ratio at surface waters.

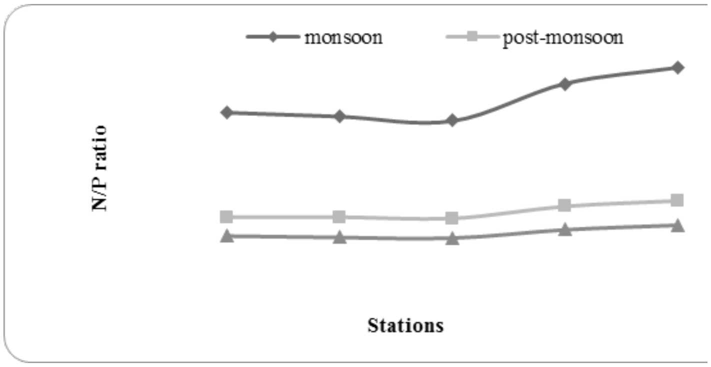

Figure 17: Distribution of N/P ratio at bottom waters.

The molar ratio of silicate to nitrate (Si/N) in surface waters ranged from 0.74 to 0.92, 1.54 to 1.94, and 3.35 to 4.20 (Figure 18) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. Similarly, Si/N ratios in bottom waters ranged from 0.75 to 1.10, 1.57 to 2.33, and 3.38 to 4.97 (Figure 19) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. Si/N ratios in surface and bottom waters showed almost constant values.

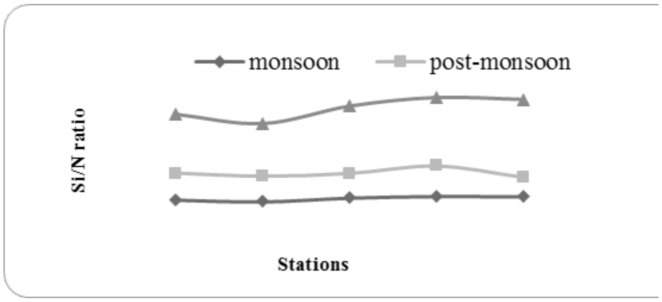

Figure 18: Distribution of Si/N ratio at surface waters.

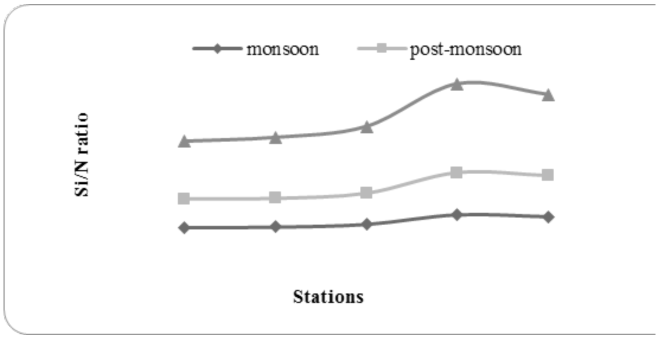

Figure 19: Distribution of Si/N ratio at bottom waters.

Chlorophyll a Concentrations

The chlorophyll a concentration in surface and bottom waters for the monsoon, post-monsoon, and pre-monsoon periods are shown in (Figures 20 and 21). Chlorophyll a concentrations in surface waters varied from 5.35 to 6.57 mg/m^3, 4.25 to 5.06 mg/

m^3, and 0.85 to 1.06 mg/m^3 (Figure 20) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average chlorophyll a content in surface waters during the monsoon, post-monsoon, and pre-monsoon periods were 6.01 ± 0.60 mg/m^3, 4.70 ± 0.10 mg/m^3, and 0.96 ± 0.10 mg/m^3, respectively. Similarly, chlorophyll a concentrations in bottom waters varied from 5.05 to 6.15 mg/m^3, 4.05 to 4.86 mg/m^3, and 0.76 to 0.98 mg/m^3 (Figure 21) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively. The average chlorophyll a content in bottom waters during the monsoon, post-monsoon, and pre-monsoon seasons were 5.63 ± 0.54 mg/m^3, 4.49 ± 0.41 mg/m^3, and 0.89 ± 0.11 mg/m^3, respectively. The average chlorophyll a content in surface and bottom waters during the monsoon and post-monsoon seasons were approximately 6.3 and 5.0 times higher, respectively, than that of the pre-monsoon season.

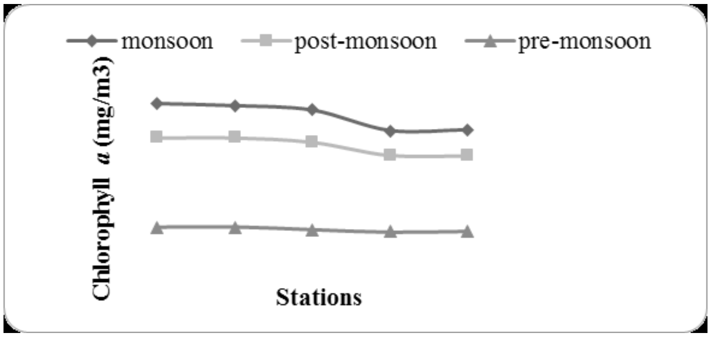

Figure 20: Distribution of chlorophyll a (mg/m^3) at surface waters.

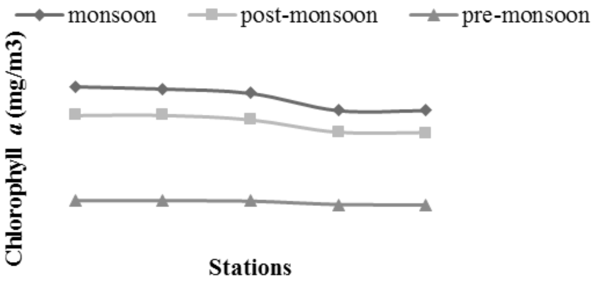

Figure 21: Distribution of chlorophyll a (mg/m^3) at bottom waters.

Discussion

The oceanographic response of the shelf waters off Cochin is linked to the seasonally reversing monsoons and the West India Coastal Currents (WICC) that are associated with the annual heating and cooling of the Asian continent [31]. Hence, the seasonal monsoon forces and continental influences play a critical role in triggering the environmental features of water column hydrography (temperature, salinity, and dissolved oxygen), which regenerates nutrients and provides structure to phytoplankton biomass (chlorophyll a concentrations) in the shelf waters off Cochin [9,16,32].

Seasonal Variations of Hydrography and Nutrients

SST ranges were lower during the monsoon (27.2 to 27.8°C) and post-monsoon seasons (28.6 to 29.2°C) compared to the pre-monsoon season (29.5 to 30.2°C). Similarly, bottom temperature ranges were lower during the monsoon (20.8 to 26.5°C) and post-monsoon seasons (21.5 to 27.8°C) compared to the pre-monsoon season (22.5 to 28.8°C). The low SST ranges noted during the monsoon and post-monsoon periods (27.2 to 27.8°C and 28.6 to 29.2°C, respectively) at the inner shelf off Cochin indicated a cooling effect that was driven by river runoff. The low bottom temperature ranges noted at the inner shelf off Cochin during the monsoon and post-monsoon seasons (20.8 to 26.5°C and 21.5 to 27.8°C, respectively) indicated a cooling effect that was induced by upwelling [6,9]. Surface water salinity ranges were lower during the monsoon (30.3 to 33.5 psu) and post-monsoon periods (30.8 to 34.0 psu), when compared to the pre-monsoon period (31.3 to 34.3 psu). The massive freshwater inputs by rivers, local precipitation, and land drainage at the inner shelf off Cochin lowered the salinity in the surface layer during the monsoon and post-monsoon periods, which established a strong salinity stratification [9,32,33]. The increased SST ranges (29.5 to 30.2°C), noted during the pre-monsoon period indicated a progressive warming effect that generated a weak thermal stratification [17,34].

The oxygen saturation in the shelf waters was regulated by advection of oxygen and the supply of organic matter, which, in turn, depended on surface runoff and in situ production [10,35]. Dissolved oxygen concentrations at the surface and in bottom waters were lower during the monsoon and post-monsoon seasons when compared to the pre-monsoon season. The surface waters were found to be oxygen deficient (O_2 = 178 to 180 µmol/l), less oxygenated (O_2 = 185 to 189 µmol/l), and oxygen undersaturated (O_2 = 190 to 196 µmol/l) during the monsoon, post-monsoon, and pre-monsoon seasons, respectively, which can be attributed to variable surface runoff during the respective periods. The low oxygen saturation during the monsoon and post-monsoon seasons coincided with high surface runoff, while the oxygen undersaturation during the pre-monsoon season coincided with low surface runoff. The large volume of fresh water that was discharged when the monsoonal rivers drained into the Cochin backwaters was carried to and spread over the inner shelf region off Cochin, which prevented vertical mixing due to density stratification, limited in air-sea gas exchanges, and made the surface waters oxygen deficient during the monsoon and post-monsoon periods [6,32]. Thus, low vertical mixing coupled with increased stratification and poor ventilation led to low oxygen saturation in the surface waters.

Hypoxic conditions (O_2 = 14 to 24 µmol/l) were prevalent in the bottom waters during the monsoon and post-monsoon seasons, primarily because of penetration of upwelled deep oceanic waters toward the bottom layers of the shelf waters off Cochin [6]. As the upwelled water advanced through the bottom layers toward the shelf region, the water would become further depleted of dissolved oxygen due to its excessive utilization fueled by high primary production and higher rate of oxidation of organic matter [24]. The increase in oxygen deficiency observed in the bottom waters from the pre-monsoon to post-monsoon and the post-monsoon to the monsoon seasons was attributed to the enhancement of nutrient and organic-matter loading from season to season off the Cochin coast. Thus, the subsurface oxygen demand that arose from the oxidation of organic matter acted as a causative factor for the intensification of the shallow hypoxic zone along the shelf waters off the west coast of India [35].

Coastal waters receive more nutrients than open ocean waters due to anthropogenic inputs from the inland freshwater sources. Rivers and streams that carry industrial, agricultural, and domestic effluents discharged from the land are rich in substances such as chemical ores, bio-fertilizers, synthetic fertilizers, synthetic detergents, and human as well as animal excreta, which are major sources of nutrients [7,36]. The slight enrichment of nitrate (approximately 1 µmol/L) and phosphate (approximately 0.8 µmol/L) in surface waters during the pre-monsoon season indicated nitrogen and phosphorus loading from anthropogenic sources on land that discharged through rivers. A similarly high enrichment of nitrate (approximately 8 µmol/L) and phosphate (approximately 1.2 µmol/L) in surface waters that were comparable to bottom water levels of nitrate (5 to 10 µmol/L) and phosphate (1 to 1.5 µmol/L) were found at stations 1, 2, and 3 during the monsoon and post-monsoon seasons. That observation indicated that apart from the upwelling of deep oceanic waters (at stations 4 and 5), substantial nitrogen and phosphorus loading was taking place on the Cochin coast as a result of riverine discharges. Similarly, the slight enrichment of silicate (approximately 4 µmol/l) at surface waters during the pre-monsoon period indicated the presence of silica loading from the weathered sediments on land that discharged through rivers. A high enrichment of silicate (approximately 7 µmol/l) in the surface waters were comparable to the levels found in the bottom waters (6 to 8 µmol/l) at stations 1, 2, and 3 during the monsoon and post-monsoon periods. That finding indicated that apart from the upwelling of deep oceanic waters (at stations 4 and 5), a substantial silica loading was also taking place on the Cochin coast as a result of riverine discharges [6].

During the monsoon and post-monsoon seasons, high nutrient-rich water persisted along with the hypoxic waters in the bottom layers. The principal reason was that the sub-thermocline water (that is, the waters below a 10m depth) in the shelf region off Cochin were a source of upwelled water that was derived from poleward undercurrents that were located in offshore waters at a depth of approximately 50 to 75m and that already had a high nutrient content [5,6,10]. Even if the upwelled waters rarely came into contact with surface waters, the shelf region off Cochin showed the presence of an excess of nutrients in the surface waters that coincided with low salinity waters, owing to its proximity to riverine or estuarine discharges [37]. Industrial effluent discharges, leakage from septic tanks, agricultural runoff, water management practices, aquaculture waste inputs, and domestic sewage inputs from the land are likely to be the cause of increased anthropogenic sources of nutrients that were observed in the shelf waters off Cochin [38]. Thus, the seasonal bio-availability of nutrients in surface waters at the shelf region off Cochin was not only largely confined from regeneration due to upwelling but was also the result of enrichment from anthropogenic sources that discharged through river runoff and land drainage.

The maximum nitrite (approximately 0.5 µmol/L) that was observed in the surface layers of oxygenated waters in the shelf region (Figure 10) was possibly due to ammonia oxidation by nitrifying bacteria [39]. Similarly, the maximum shallow nitrite (1.68 to 2.95 µmol/L) observed in bottom layers (Figure 11), which demonstrate an association with hypoxic waters that had a greater intensity toward the inner shelf regions, was due to denitrification [10]. Thus, the moderate nitrification in surface waters coupled with denitrification in bottom waters at the shelf regions can lead to an increase in the emissions of greenhouse gases into the atmosphere, such as nitrous oxide [35,40].

Eutrophication and Biological Response

Eutrophication is a process by which water bodies become more eutrophic through the addition of increased nutrients from external sources [1]. The seasonal distribution of chlorophyll a showed higher concentrations at surface layers than bottom layers due to nutrient enrichment that occurred largely through river runoff rather than upwelling [6,7]. Based on the relative magnitude of nutrient inputs and the corresponding increase in chlorophyll a concentrations, the trophic status of coastal marine ecosystems can be broadly classified into oligotrophic (< 1 mg/m^3), mesotrophic (1-3 mg/m^3), eutrophic (3-5 mg/m^3), and hypertrophic (> 5 mg/m^3) waters [1]. Accordingly, during the monsoon season, the surface waters were highly enriched with nutrients ($NO_3 \geq 4$ µmol/L, $PO_4 \geq 1.2$ µmol/L, and $SiO_4 \geq 6$ µmol/L), and they were found to be hypertrophic (chlorophyll a ≥ 5 mg/m^3) due to enormous river runoff. During the post-monsoon season, the surface waters were moderately enriched with nutrients ($NO_3 \geq 2$ µmol/L, $PO_4 \geq 1$ µmol/L, and $SiO_4 \geq 4$ µmol/L), and they were found to be eutrophic (chlorophyll a = 4 -5 mg/m^3) due to elevated river runoff. During the pre-monsoon season, the surface waters were slightly enriched with nutrients ($NO_3 \geq 1$ µmol/L, $PO_4 \geq 0.8$ µmol/L, and $SiO_4 \geq 2$ µmol/L), and they were found to be oligotrophic (chlorophyll a ≤ 1 mg/m^3) due to low river runoff.

Trichodesmium or *Noctiluca* blooms (red tides) frequently occur in the shallow, warm, continental shelf waters off the west coast of India, and they are probably linked to the coastal eutrophication phenomena that has been initiated by increased anthropogenic additions of nutrients from land that is associated with freshwater discharges through the rivers [7,10]. With nutrient enrichment, a shift in the composition of the plankton community is frequently observed, with large diatoms giving way to smaller cyanobacteria and small flagellates. The primary nutrient that regulates the shift in phytoplankton community structure from diatoms to flagellates is silicate [41]. The riverine nutrient fluxes with more nitrate than phosphate may potentially lead to a limitation in phosphorus for phytoplankton production in the coastal waters of India [7]. However, the phosphorus deficiency is effectively maintained as regenerated phosphate, which is readily available in the shelf waters off Cochin through upwelling during the monsoon and post-monsoon seasons when nitrogen-fixing plankton begin to appear [21]. The depth-wise nutrient distribution in this region is such that vertical mixing brings up substantial amounts of nitrate and phosphate to the euphotic zone, but not much silicate, thereby limiting diatom productivity [6]. The nitrate and phosphate enrichment may lead to a deficiency of dissolved silicate, which limits diatom growth. A decrease in the Si/N ratio below 1 at surface waters during the monsoon period (Figure 18) is expected to cause a shift in the phytoplankton community structure from diatoms to coccolithophores and dinoflagellates, which probably leads to the formation of red tides in this region [22]. Many of these species can be harmful to higher trophic levels, and can thereby disrupt normal ecosystem function. The dominance of such species results in a failure of normal predator–prey interactions, which, in turn, enhances the transfer of nutrients that sustain the blooms at the expense of competing algal species. Because the riverine nutrients accelerate coastal eutrophication at the shelf waters off Cochin, there exists a critical need to understand the quantitative linkages that exist between nutrient inputs through anthropogenic activities at the Vembanad Lake riverine catchments and their coastal ecosystem effects.

Conclusion

The present study demonstrated an extreme seasonality in the biological responses of the Cochin coastal waters to additional nutrients. This was caused by rivers, which was evident by the fact that a slight increase in the bioavailability of nutrients that arose from anthropogenic sources on land between the pre-monsoon, post-monsoon, and monsoon seasons, even at low concentrations, had the ability to enhance the chlorophyll a concentrations. The elevated levels of chlorophyll a noted during the monsoon and post-monsoon seasons indicate a high risk of eutrophication events at the shelf waters off Cochin, probably due to nutrient enrichments (N and P loading) that are mainly caused by industrial effluent discharges, agricultural run-off, septic tank leakages, aquaculture waste inputs, and domestic sewage inputs through the rivers. Hence, in view of the projected population growth and owing to changes in land-use patterns for industrialization, urbanization and agricultural expansion, in the future, a drastic increase in the bioavailability of river-borne anthropogenic nutrients that is expected to be released from the Vembanad Lake riverine catchments might further increase and accelerate the eutrophication and hypoxic events in the coastal marine environment off Cochin.

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