Water quality status of Cochin estuary, India

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In the present study the water quality of the Cochin estuary was monitored from June 2009 to May 2011. The depth of the Cochin estuary was found to be reduced. Range of water temperature showed an increasing trend. Salinity of the estuary showed oligo-mesohaline nature. TDS established a strong positive correlation significant at 1% level between river discharge and conductivity. Higher oxygen concentration during post-monsoon period was due to the higher primary production occurring in the surface layers during this period. Elevated levels of CO2 and pH shifting to alkaline side indicate ecosystem stress. Organic pollution and nutrient enrichment in the Cochin estuary is attributed to the high BOD values (>5mg L⁻¹). Average concentration of ammonia-N increased. The heavy rainfall and the increased surface runoff during the monsoon attributed to the high values of silicate in the surface waters during monsoon period. In the Cochin estuary the season wise, zone wise and year wise analysis of Redfield ratio showed a nitrogen limiting condition.

[Key words: Cochin estuary, Water quality, Nutrients, Dissolved Oxygen]

Introduction

Estuaries in the worldwide are being exposed to an increasingly complex suite of environmental perturbations such as nutrient enrichment, organic carbon loading, chemical contaminants, habitat loss and alterations, overfishing, freshwater diversions and introduced species, originating from overpopulation and uncontrolled development in coastal watersheds, as well as human activities in the estuarine embayment themselves. At the same time, demand for water for varied purposes such as residential usage, agriculture, industrial usage, etc has increased. The environmental effects of these changes are directly reflected in the parameters of water quality. The city of Kochi, situated along the west coast of India, the business and industrial hub of Kerala, and also a hot spot for coastal pollution. Indiscriminate use of fertilizers, insecticides, fungicides and municipal waste has caused considerable damage to the water quality of estuary. Estuary receives 104 × 10^3 m³ of industrial waste and 260 m³/day of untreated sewage from Kochi city, besides large quantities of waste from agricultural and aquatic farms. Case studies of eutrophication and hypoxia have been reported from the Kochi estuary as well as the Kodungallur-Azhikode estuary. Several incidents of fish mortality has been reported in the Cochin estuary, caused by indiscriminate discharges. The present work assessed the water quality variation in Cochin estuary for the period 2009-2011.

Materials and Methods

The Cochin estuary is a part of the Vembanad-Koll Wetlands, which is the third largest coastal wetland system in India (9°47'31" - 10° 12'N latitude and 76° 9'25" - 76° 24'28" E longitude). Monthly field sampling was conducted for 24 months, from June 2009 to May 2011, in nine selected stations of the Kochi estuary (Fig. 1). Kochi estuary is a monsoonal estuary in which the river discharge exhibits large seasonal variation. Estuary was classified into three zones based on the salinity regime based on the location. Northern zone of the estuary was represented by stations 6, 7, 8 and 9; stations 2 and 3 were clustered into southern zone while stations 1, 4 and 5 were demarcated as central.
The southern zone and central zones were mesohaline (5-18 ppt) and the northern zone was oligohaline (0.5-5 ppt) according to the Venice System of classification (1959).

The surface water samples were collected using a plastic bucket and bottom water samples were collected using a standard Niskin sampler (General Oceanics) of 5L capacity. Depth was measured in the field by a graduated weighted rope until it touches the bottom. Atmospheric and water temperature were determined on field by standard degree centigrade mercury thermometer with an accuracy of ± 0.01°C. Transparency of the water body was measured using Secchi disc. Salinity was measured by Mohr-Knudsen method. Total dissolved solids (TDS) and conductivity were measured using Systronics water analyser (Model No. 371; accuracy± 0.01) calibrated with standard sea water. Turbidity was measured using Nephelo– Turbidity meter – Systronics model no: 132. Dissolved oxygen was estimated by the modified Winkler method. pH measurements were made using a portable pH meter (Systronics model No: 371; accuracy ± 0.01). Free carbon dioxide and total alkalinity were analysed using the titrimetric method. Total hardness was determined using the EDTA titrimetric method. Biological oxygen...
demand (BOD) was determined \(^{16,19}\). Ammonia-nitrogen was analyzed using the phenate method\(^{15}\). Nitrite-nitrogen was measured using the diazotised method\(^{15}\). Nitrate-nitrogen was estimated using the resorcinol method\(^{20}\). Dissolved inorganic phosphate-phosphorus was measured using the ascorbic acid method\(^{14,15}\). The dissolved silicate-silicon in the water was estimated using the molybdisilicate method\(^{15}\). Sulphide in the water sample was determined as hydrogen sulphide, spectrophotometrically following the Cline method (1969) \(^{15}\).

Statistical analysis two-way ANOVA (Analysis of Variance), standard deviation and correlation was done based on SPSS.22 software packages for Windows for

![Fig. 2—Distribution of (A) Salinity, (B) Dissolved oxygen, (C) pH, (D) Ammonia-nitrogen, (E) Nitrite-nitrogen, (F) Nitrate-nitrogen, (G) Phosphate-phosphours, (H) Hydrogen sulphide in Cochin estuary during 2009-11 period.](image-url)
testing the presence of significant differences and correlation among the parameters between stations and between seasons. The PRIMER v 6 (Plymouth Routines in Multivariate Ecological Research, version 6.1.9), was used for Cluster analysis of data. SURFER.11 and ORIGIN 8.5 were used for data analyses and graphical representation of data.

**Results and Discussion**

The entire estuary was shallow in nature with an average depth of 3.67 ± 0.39 m. In the present study the depth ranged from 0.10 m at station 9 to 8.50 m at station 1. Central zone of the estuary was found to be deeper compared to the other zones, which may be due to the dredging activities in the area. The variation of depth in the annual range was 0 to 8.50 m during the 2009-10 period and 0.80 m to 7m during 2010-11 period. Mean monthly variation of depth showed the minimum (0.10 m) in July 2009 and maximum (8.50 m) in December 2009. ANOVA result of depth showed that it was significant at 1% level between seasons (p≤0.05), between stations (p≤0.001), between seasons and stations (p≤0.05). Average depth of the Vembanad lake reduced from 6.7m to 4.4m in the past 50 years from the 1930s to 1980s. In the present study the depth was found to be further reduced to a value of 3.67m. Shallowness reduced the drainage capacity of the lake from 2.4 km$^3$ to 0.6 km$^3$, a decline of 75% caused by river discharge and the tidal influx has led to the decrease in the depth of the estuary.

The mean atmospheric temperature of the Cochin estuary was 28.52 ± 1.43 °C. Zone wise variation of atmospheric temperature was lower in the southern zone (27.72 ± 0.46 °C) of the estuary. Atmospheric temperature showed slight variations between the seasons. It was higher during pre-monsoon period (29.04 ± 0.56 °C) and lower during monsoon period (27.93 ± 0.56 °C). Annual variation of atmospheric temperature showed that the 2009-10 period was hotter (29.21 ± 1.34 °C) compared to the 2010-11 period (27.84 ± 1.21 °C). ANOVA result of atmospheric temperature observed that it was significant at 5% level between stations (p≤0.001).

The surface water temperature ranged from 34.00 °C (station 8 and 9) to 25.00 °C (stations 8 and 9), whereas the bottom water temperature varied from 33.00 °C (station 9) to 25.00 °C (station 5). Higher water temperature in the Narmada estuary (29-30 °C) and Mahi estuary (28-30 °C) compared to Sabarmati estuary (27-30 °C) could be attributed to the release of industrial waste. Monthly mean values of temperature were found to be more or less similar throughout the study period. Maximum average temperature during 2009-10 period was recorded in May 2010 (32.04 °C) and that in 2010-11 was 31.33 °C in May 2011. Average water temperature was lowest during the monsoon period. The mean temperature during the pre-monsoon period was highest for the surface and bottom waters across all the stations. Monthly variations of water temperature showed a decline in temperature as the southwest and northeast monsoon period progresses, which attain the peak in the months of October and May. The zone wise variation of water temperature was maximum in the southern zone (29.34 ± 0.22 °C) and minimum in the northern zone (29.17 ± 0.18 °C). ANOVA result of water temperature showed that it was significant at 1% level between seasons (p≤0.001), between seasons and stations (p≤0.001). A positive correlation significant at 1% level emerged between water temperature and atmospheric temperature ($r^2$=0.594).

A strong negative correlation significant at 1% level between the water temperature and river discharge ($r^2$= -0.578)

Transparency values were generally low (0.61 ± 0.15 m) in the estuary, especially during the monsoon period. It was higher during the post-monsoon period (0.90 ± 0.15 m) and the pre-monsoon period (0.81 ± 0.15 m). The reduction in the values during the monsoon period was due to the decrease in solar radiation and the increase in river runoff. Mean station wise values showed that transparency was lowest at station 4 (0.55 m) and highest at station 8 (1.14 m). The transparency values were higher during the 2009-10 period (0.82 m) in comparison to the 2010-11 period (0.73 m). ANOVA result of transparency of the water body showed that it was significant at 1% level between seasons (p≤0.001), between stations (p≤0.001), between seasons and stations (p≤0.01). The zone-wise distribution of transparency in the Cochin estuary showed that the transparency was higher in the upstream regions, where the salinity was the lowest. Secchi disc depth in the estuary (0.10 to 1.90 m) was lower compared to the earlier records in Cochin estuary (0.5 to 2m). A similar value was observed in the Bahia Blanca estuary in the south-western Atlantic Ocean (0.26 to 1.15m). It showed a strong negative correlation significant at 1% level between the rainfall ($r^2$= -0.542) and river discharge ($r^2$=-0.531). Similar observation was made in the Gambia River estuary in West Africa.
Africa

Salinity values showed wide variations from 0.01 ppt to 34 ppt in the surface and bottom waters. Higher salinity in the bottom water compared with the surface water was due to sea water intrusion from the Arabian Sea. Salinity showed a definite trend from the southern zone to the northern zone, where it was found to be decreasing. Corresponding to the highest amount of rainfall received during the monsoon period season, salinity was found to be the lowest. Annual mean values of salinity were comparatively lower (6.81 ± 3.86 ppt) during the 2010-11 period compared to the 2009-10 period (7.88 ± 4.70 ppt).

Annual rainfall and river discharge was high during 2010-11 period (4109.10 mm and 285050.517 m$^3$/s) compared to 2009-10 period (3314.20 mm, 217606.792 m$^3$/s). Station wise mean value of salinity was maximum at station 1 (16.18 ppt) and minimum at station 8 (0.93 ppt). In the present study, salinity of the Cochin estuary as was oligo-mesohaline in nature. Salinity of the central and southern zones of the estuary was mesohaline (5-18 ppt) in nature while the northern zone was oligohaline in nature (0.5-5 ppt). Gradual increase in salinity from the head towards the mouth of the system is a typical estuarine character. This characteristic was observed in the Cochin estuary from the southern zone to the northern zone. Fresh water condition (<0.5 ppt) prevailed during the monsoon period months in most of the stations except stations 1 and 2. ANOVA of salinity was significant at 1% level between seasons ($p \leq 0.001$), between stations ($p \leq 0.001$), between seasons and stations ($p \leq 0.01$) whereas it was significant at 5% level between surface and bottom waters ($p \leq 0.05$). A positive correlation ($r^2 = 0.523$) significant at 1% level between transparency and salinity and a strong negative correlation ($r^2 = -0.430$) with turbidity significant at 5% level were established. The TDS value of surface waters was observed to be maximum at station 5 (323.00 ppm) and minimum at station 9 (0.01 ppm). For bottom waters, TDS was maximum at station 5 (318.00 ppm) and minimum at station 8 and station 9 (0.02 ppm). Mean annual TDS was found to be very high (30.18 ppm) during 2009-10 period compared to 2010-11 period (6.30). ANOVA of TDS was significant at 1% level between seasons ($p \leq 0.001$). Total dissolved solids established a strong positive correlation significant at 1% level between river discharge ($r^2 = 0.525$), conductivity ($r^2 = 0.962$). A positive correlation significant at 5% level between rainfall ($r^2 = 0.504$) and turbidity ($r^2 = 0.416$) was observed. A negative correlation significant at 5% level emerged between the TDS and depth ($r^2 = -0.458$) as well as between TDS and alkalinity ($r^2 = -0.490$).

Station wise mean value of conductivity was the highest at station 5 (50.62 ± 12.46 mS) and lowest at station 2 (14.25 ± 12.46 mS). The highest conductivity (34.10 ± 6.11 mS) was recorded from the northern zone and lowest conductivity (22.37 ± 6.11 mS) was recorded from the southern zone. In 2009-10 period, the mean annual conductivity was (52.08 mS) and it was 8.97 mS observed during the 2010-11 period. ANOVA of conductivity was significant at 1% level between seasons ($p \leq 0.001$). Conductivity showed positive relationship with river discharge ($r^2 = 0.425$) significant at 5% level; a negative correlation ($r^2 = -0.495$) significant at 5% level was with alkalinity.

High turbidity values were observed in the estuary with an average of 8.65 ± 5.42 NTU, with the peak concentration occurring during southwest monsoon period (14.66 ± 5.23 NTU). The southwest monsoon period results in a turbulent condition, favouring the resuspension of the bottom sediment by tidal stirring action. Highest mean turbidity value was observed at station 3 (13.51 NTU) and the lowest was observed at station 8 (4.25 NTU). Turbidity was low near the mouth of estuary, with its excess sea water, and increased toward inland with distance. Bottom waters were found to be more turbid than the surface waters. Southern zone (12.89 NTU) was more turbid compared to the other zones. Mean annual variation of turbidity showed the peak (9.39 NTU) during 2010-11 period. ANOVA of turbidity was significant at 1% level significance between seasons ($p \leq 0.001$), between stations ($p \leq 0.001$), between surface and bottom waters ($p \leq 0.01$). Turbidity showed a strong positive correlation with rainfall ($r^2 = 0.730$) and river discharge ($r^2 = 0.677$) significant at 1% level. A negative correlation ($r^2 = -0.450$) with 5% level of significance emerged between alkalinity and turbidity.

The average dissolved oxygen in the Cochin estuary was 6.20 ± 0.89 mg L$^{-1}$ during the period of the study. Dissolved oxygen values were higher in the surface waters of the estuary. Mean station wise value was maximum at station 9 (6.88±0.36 mg L$^{-1}$) and minimum at station 3 (5.81±0.36 mg L$^{-1}$). The
dissolved oxygen concentration was higher in the northern zone (6.42 ± 0.29 mg L⁻¹) of the estuary and lower in the southern zone (5.87 ± 0.29 mg L⁻¹) of the estuary. Solubility of oxygen in water decreases with increased temperature and salinity. The high amount of dissolved oxygen in the northern zone might be due to the prevalence of low saline conditions, attributed to the high solubility of oxygen. Dissolved oxygen values were found to be lower during the pre-monsoon period (5.55 ± 0.59 mg L⁻¹) and higher during the post-monsoon period (6.70 ± 0.59 mg L⁻¹). Higher oxygen concentration during post-monsoon period was due to the higher primary production occurring in the surface layers during this period. The dissolved oxygen values during the post-monsoon period might be due to the higher solubility of oxygen in colder and less saline water. The ANOVA result of dissolved oxygen showed that variations between seasons (p ≤ 0.001) and between stations (p ≤ 0.001) were significant at 1% level. In the present study, approximately 16% of the samples exhibited a dissolved oxygen concentration ≤ 5 mg L⁻¹, indicating a biologically stressed condition in the estuary. Depletion of dissolved oxygen was due to the upwelled propagation of high saline water mass and its increased residence time in the lower estuary. Dissolved oxygen showed a negative correlation with the light attenuation coefficient at 5% level (r² = -0.436).

pH was found to be more or less uniform throughout the study period. The vertical gradient of the pH was less significant in the estuary. Surface water pH ranged from 8.90 at station 6 to 4.21 at station 9. The bottom water pH ranged from 8.45 at station 2 to 3.35 at station 9. Average pH of the Cochin estuary was generally on an alkaline side (7.25 ± 0.40). During post-monsoon period the pH values were highest (7.47 ± 0.21) followed by pre-monsoon period (7.21 ± 0.21) and monsoon period (7.07 ± 0.21). Addition of CO₂ to water will cause the pH to decrease due to the formation of hydrogen ions by the ionisation of carbonic acid. Similarly, the removal of carbon dioxide from the system would lead to a rise in pH. The pH was high during the post-monsoon period due to the high photosynthetic activity which removes CO₂ from water and the low solubility of gases due to high water temperature. The low pH during monsoon period was due to the opposite conditions. A gradual decrease in pH from the marine waters of station 1 (7.66 ± 0.36) to the fresh water at station 9 (6.60 ± 0.36) was evident during all the seasons of the year. However, the peak monsoon period was marked by heavy rains and land runoff, the pH values tended to fall in all the stations of the estuary. As a result pH value shifted for a brief acidic phase during the monsoon period of 2010-11. Northern zones (6.92 ± 0.34) of the estuary were slightly acidic in nature while the southern zone (7.49 ± 0.34) and the central zone (7.52 ± 0.34) were on the alkaline side. Streams and rivers transporting large quantities of humic materials in colloidal suspension are frequently of a slightly acidic nature. Upon meeting sea water, the colloidal particles coagulate and the pH shifts towards the alkaline side. Another reason might be the discharge of industrial effluents. High pH in the marine zone was on account of the intrusion of sea water and low values in riverine zone that could be due to the influence of freshwater and effluents introduced through various sources. Mean month wise variations in pH ranged from 4.51 in July 2010 to 8.50 in July 2009. The annual variations in pH showed a slightly higher pH in 2009-10 period (7.29 ± 0.33) compared to 2010-11 period (7.20 ± 0.48). ANOVA of pH was significant at 1% level between seasons (p ≤ 0.001) and between stations (p ≤ 0.001). A positive correlation significant at 1% level was observed between transparency (r² = 0.564; r² = 0.613) and salinity, while a negative relation significant at 5% level between pH and turbidity (r² = -0.415)

Station wise mean values of dissolved showed the maximum at station 3 (9.35 ± 0.87 mg L⁻¹) and minimum at station 7 (7.28 ± 0.87 mg L⁻¹). The dissolved carbon dioxide values were found to be higher in the central zone (8.60 ± 0.40 mg L⁻¹) and lower in the northern zone (7.81 ± 0.40 mg L⁻¹). The free carbon dioxide was higher during the monsoon period (8.47 ± 0.39 mg L⁻¹) and lower during the pre-monsoon period (7.75 ± 0.39 mg L⁻¹). Mean annual values of carbon dioxide were 9.07 ± 1.24 mg L⁻¹ during the 2009-10 period and 7.31 ± 2.19 mg L⁻¹ during the 2010-11 period. ANOVA of free carbon dioxide showed that it was significant at 1% level between stations (p ≤ 0.01). For good fish production, a free carbon dioxide concentration level less than 5 mg L⁻¹ is recommended. In the Cochin estuary, carbon dioxide values were high with an average of 8.19 mg L⁻¹. The consequences of global climate change include elevated levels of carbon dioxide and decrease in pH affect the equilibrium of inorganic
carbon complexes in the estuary such as carbonates, bicarbonates. Shift in CO$_2$/HCO$_3^-$ ratio may benefit species able to utilise only CO$_2$ by diffusive uptake, but most phytoplankton species have an active uptake system for inorganic carbon. In the present study the carbon dioxide values were found to be elevated but the pH is shifting towards an alkaline side.

The average alkalinity value of the Cochin estuary was 36.26 ± 14.32 mg L$^{-1}$ during the study period. Bottom waters showed higher alkalinity values during the study period. Average alkalinity of the Cochin estuary (36.26 ± 14.32 mg L$^{-1}$) was comparable with the Kodungallur-Azhikode estuary, 35.1 ± 18.4 mg L$^{-1}$ 9,26. The mean station wise value of alkalinity was maximum at station 1 (47.77 ± 8.31 mg L$^{-1}$) and minimum at station 9 (24.86 ± 8.31 mg L$^{-1}$). Alkalinity values were found to be higher in the central zone (42.46 ± 7.62 mg L$^{-1}$) and lower in the northern zone (28.90±7.62 mg L$^{-1}$). Relatively high alkalinity was observed during the post-monsoon period (40.22 ± 5.09 mg L$^{-1}$), when compared to the pre-monsoon period (38.05 ± 5.09 mg L$^{-1}$) and monsoon period (20.05 ± 5.09 mg L$^{-1}$). The alkalinity was observed to be higher (41.45 ± 14.25 mg L$^{-1}$) during 2010-11 period. The ANOVA of alkalinity showed that variations between seasons (p≤0.001), between stations (p≤0.001) were significant at 1% level whereas it was significant at 5% level between seasons and stations (p≤0.05).

The average total hardness of the estuary was 1823.29 ± 1596.76 mg L$^{-1}$. Total hardness of the bottom waters was higher in comparison with the surface waters. Station wise mean value was highest at station 1 (3233.85 mg L$^{-1}$) and lowest at station 9 (61 mg L$^{-1}$). Total hardness of the estuary drastically decreased during monsoon period of the 2010-11 period. Total hardness was higher during the 2009-10 period (1906.96 ± 1287.82 mg L$^{-1}$). ANOVA of total hardness was significant at 1% level between seasons (p≤0.001) and between stations (p≤0.001) where as it was significant at 5% level between surface and bottom waters (p≤0.05). Pearson correlation analysis showed a negative relationship between rainfall ($r^2= -0.412$) and river discharge ($r^2= -0.475$) at 5% level; where as a positive relationship with water temperature ($r^2= 0.542$) at 1% level.

The average biological oxygen demand (BOD) during the present study was 2.42 ± 1.53 mg L$^{-1}$. Surface waters showed the highest biological oxygen demand values. Mean station wise value of BOD was the highest at station 5 (3.15 ± 0.37 mg L$^{-1}$) and lowest at station 7 (1.89 ± 0.37 mg L$^{-1}$). Maximum BOD was recorded in the central zone (2.67 ± 0.23 mg L$^{-1}$) and minimum in the northern zone (2.22 ± 0.23 mg L$^{-1}$). Among the seasons, BOD was higher during the monsoon period (2.91 ± 0.43 mg L$^{-1}$) as compared to the post-monsoon period (2.12 ± 0.43 mg L$^{-1}$) and pre-monsoon period (2.22 ± 0.43 mg L$^{-1}$). Mean annual values of BOD was higher during 2009-10 period (2.44 ± 1.70 mg L$^{-1}$) compared to 2010-11 period (2.40 ± 1.42 mg L$^{-1}$). ANOVA of BOD was significant at 1% level between seasons (p≤0.001).

The average value of ammonia-nitrogen in the Cochin estuary was 11.48 ± 8.02 μmol L$^{-1}$. Ammonia values ranged from 0.35 μmol L$^{-1}$ to 59.03 μmol L$^{-1}$. In the present study, the average concentration of ammonia (11.48 μmol L$^{-1}$) was very high compared to the earlier observation 0.34±0.30 μmol L$^{-1}$. The presences of higher levels of ammonia indicate the increased sewage input and agricultural runoff into the surface waters. Minimum value of 0.35 μmol L$^{-1}$ was recorded at station 8 in August 2009 and the maximum value of 59.03 μmol L$^{-1}$ was at station 2 in April 2011. Ammonia-nitrogen values were found to be comparatively higher at station 9 during the entire study period. In the northern zone, surface waters contain more ammonia than the bottom waters, while the central and southern zones have higher concentrations in the bottom waters. The ammonia-nitrogen values were higher in the northern zone (13.85 ± 2.46 μmol L$^{-1}$) of the estuary. In the central zone, the concentration of ammonia was high (10.20 μmol L$^{-1}$) at station 5 and low at station 1. In the southern zone, the station 3 showed higher value (10.99 μmol L$^{-1}$) compared to station 2 (9.23 μmol L$^{-1}$). It was higher during the 2010-11 period (12.21 ± 10.16 μmol L$^{-1}$) and the maximum was recorded during the pre-monsoon period (13.45 ± 2.36 μmol L$^{-1}$). Apart from industrial waste, regeneration and excretion are the other sources of ammonia into the estuary. High concentration of ammonia during the pre-monsoon period is contributed by the excretion of zooplankton and the members of higher trophic levels. ANOVA result observed that the variations were significant between seasons (p≤0.01) and stations (p≤0.001) whereas it was significant at 5% level between seasons and stations (p≤0.05).

Average nitrite-nitrogen of the estuary was 0.72 ± 0.43 μmol L$^{-1}$. The nitrite-nitrogen content
of the bottom waters was higher in most of the stations. Mean station-wise values ranged from 0.43 ± 0.26 μmol L⁻¹ at station 8 to 1.10 ± 0.26 μmol L⁻¹ at station 3. The nitrate-nitrogen was higher in the southern zone of the estuary (1.07 ± 0.29 μmol L⁻¹). It was higher during the pre-monsoon period (1.01 ± 0.28 μmol L⁻¹) and lower during the post-monsoon period (0.45 ± 0.28 μmol L⁻¹). The peak obtained during the pre-monsoon period indicates that the hydrodynamic processes associated with sea water intrusion control the nitrite concentration. Annual distribution of nitrite-nitrogen showed that it was higher during the 2009-10 period (0.79 ± 0.50 μmol L⁻¹) than the 2010-11 period (0.65 ± 0.37 μmol L⁻¹). Variations between seasons (p≤0.001) and between stations (p≤0.001) were significant at 1% level. Dissolved nitrate-N showed a negative correlation (r² = 0.511) significant at 5% level with dissolved oxygen. Nitrification is influenced by dissolved oxygen. However, the nitrification process can still function at very low concentrations of dissolved oxygen.

Average nitrate-nitrogen of the estuary was 13.12 ± 10.54 μmol L⁻¹. The nitrate-nitrogen content of the bottom waters was higher in most of the stations. Nitrification is most likely restricted to the bottom sediments, which have been suggested as a major source of nitrate to the water column of tropical estuaries. Mean station-wise values of nitrate-nitrogen ranged from 9.84 ± 2.24 μmol L⁻¹ at station 1 to 16.16 ± 2.24 μmol L⁻¹ at station 9. Nitrate-nitrogen values were higher in the southern zone (13.40 ± 0.24 μmol L⁻¹) of the estuary and lower in the northern zone (12.92 ± 0.24 μmol L⁻¹). It was higher during the monsoon period (22.42 ± 8.49 μmol L⁻¹) compared to the other seasons. Concentration of nitrate-N was highest during the monsoon period because the concentration entirely depends upon the freshwater discharge and land runoff. The concentration was influenced slightly by the intrusion of saline water. ANOVA result of nitrate-nitrogen was significant at 1% level between seasons (p≤0.001) and was significant at 5% level of significance between stations (p≤0.05) and between seasons and stations (p≤0.05). Mean annual nitrite + nitrate (dissolved inorganic nitrogen (DIN) = (nitrite + nitrate) + ammonium) concentration accounts for approximately 55% of DIN, whereas ammonia contributes the remaining 45% in the estuary. Ammonia accounts for approximately 36% of the DIN in the Godavari estuary. Nitrate-N showed a strong positive correlation significant at 1% level between rainfall (r² = 0.597), river discharge (r² = 0.660), turbidity (r² = 0.572), conductivity (r² = 0.760) and TDS (r² = 0.810). A weak positive correlation was established with the light attenuation coefficient (r² = 0.460). A negative correlation significant at 1% level was observed with water temperature (r² = 0.500) and transparency (r² = 0.518).

Comparatively higher content of phosphate-phosphorus was observed in the bottom waters as compared to the surface waters. Average phosphate-phosphorus of the estuary was 7.38 ± 8.18 μmol L⁻¹. Mean station wise values were observed to be highest at station 9 (11.85 ± 1.79 μmol L⁻¹) and lowest at station 1 (5.96 ± 1.79 μmol L⁻¹). Phosphate-phosphorus was higher in the northern zone of the estuary (8.23 ± 0.88 μmol L⁻¹). Industrial effluent discharge and domestic sewage containing detergents and fertilizers used in the agricultural fields in this zone significantly influenced the nutrient concentration. The same observation was reported from the Bahia Blanca estuary in Argentina while studying the effects of sewage pollution on mesozooplankton. Phosphate-phosphorus showed a threefold increase during the pre-monsoon period (12.22 ± 4.19 μmol L⁻¹) in comparison with the post-monsoon period (5.10 ± 4.19 μmol L⁻¹) and monsoon period (4.83 ± 4.19 μmol L⁻¹). Mean monthly variation ranged from 44.27 μmol L⁻¹ in February 2010 to 0.13 μmol L⁻¹ in April 2010. Inter-annual variation showed that it was higher (9.26 μmol L⁻¹) during the 2009-10 period compared to the 2010-11 period (5.51 μmol L⁻¹). Phosphate variations were significant at 1% level between seasons (p≤0.001).

The average value of silicate-silicon in the Cochin estuary was 32.53 ± 11.82 μmol L⁻¹. Mean station wise values ranged from 41.83 μmol L⁻¹ (station 8) to 22.71 μmol L⁻¹ (station 1). At most stations, the surface water contains more silicate than the bottom water. Silicate-silicon values were found to be higher during the monsoon period (37.50 ± 4.32 μmol L⁻¹), which may be due to the heavy land runoff. Heavy rainfall and the increased surface runoff during the monsoon period contributed to the higher values of silicate in the surface waters during the monsoon period. Mean monthly values showed maximum (83.07 μmol L⁻¹) in July 2009 at station 4 and minimum (1.44 μmol L⁻¹) in July 2010 at station 7. Silicate-silicon values were higher (37.36 ± 10.99 μmol L⁻¹)
during the 2009-10 period. ANOVA result of silicate showed that it was significant at 1% level between seasons (p≤0.001), between stations (p≤0.001) and between seasons and stations (p≤0.001).

The average sulphide concentration of the Cochin estuary was 20.84 μmol L⁻¹. The sulphide was found to be very high in the bottom waters of the estuary. Mean station-wise values ranged from 5.91 μmol L⁻¹ at station 7 to 27.76 μmol L⁻¹ in station 3. It was higher (22.77 ± 3.57 μmol L⁻¹) in the northern zone of the estuary and lower (16.40 ± 3.57 μmol L⁻¹) in the central zone of the estuary. It was drastically high (50.18 ± 26.24 μmol L⁻¹) during the monsoon period. Mean monthly variation of sulphide ranged from 0 to 885.31 μmol L⁻¹ in September 2010 at station 6. The variations of hydrogen sulphide between seasons was significant at 1% level whereas the interaction between seasons and stations (p≤0.05), and significant at 5% level between stations and surface and bottom waters (p≤0.05) and between seasons and surface and bottom waters (p≤0.05). The equilibrium between hydrogen sulphide, hydrosulphide and sulphide is determined by the pH. If the pH is less than 10, it is not detrimental to the ecosystem 45. Sulphide showed a positive correlation significant at 1% level between Rainfall (r² = 0.562), river discharge (r² =0.535) and turbidity (r² = 0.594) and weak correlation with attenuation coefficient. It also showed a negative correlation significant at 5% level with atmospheric temperature (r² = 0.448); water temperature (r² = 0.514); transparency (r² = 0.477) and total hardness (r² = 0.495).

The N:P ratio of Redfield has long been used to estimate which of these nutrients is limiting the growth of algae in aquatic systems. Station-wise mean values of Redfield ratios ranged from 0.01 at Station 5, 6 and 7 to 5.10 in station 8. Mean Redfield ratio was found to be higher during monsoon period (0.65) and lower during post-monsoon period (0.40). Maximum photosynthetic activity during post-monsoon period resulted in a low Redfield ratio. A Redfield ratio less than one indicates the complete exhaustion of nitrate. Redfield ratio of Vellar estuary showed high values during monsoon period and post-monsoon period, and a low value in summer 46. A similar result was observed in the present study. Ratios of inorganic N:P (by atoms) ranged from 1:1 to 99:1 during the year 40. Average N:P ratio of the Kodugallur-Azheekode estuary was 21.91. Additionally, the estuary was phosphorus-limited during monsoon period and nitrogen limited during post and pre-monsoon periods 9. In the Cochin estuary the season wise, zone wise and year wise analysis of Redfield ratio showed a nitrogen limiting condition. This means N:P<10 and Si:N>1,indicating N limitation 47,48, 49. The direct application of the Redfield ratio in estuarine systems is problematic. Measurements of limiting nutrients are typically problematic due to the rapid regeneration of nutrients and short turnover times in an estuarine system 50.

Cluster analysis

The station wise dendrogram showed four clusters (Fig. 3). Bottom waters of the first, second and fourth
stations form a cluster, while the surface waters of these three stations form another cluster. These cluster formation is justified by the similar environmental conditions. The bottom water of station 6 was distinct compared to all the other stations. Surface waters of station 3 and 5 form a cluster and the bottom waters form another cluster. Solid line reflects significant differences between clusters and dotted line reflect no statistical evidence for the substructures within the group. Two solid lines in the dendrogram shows that the surface and bottom waters of the central and southern zones of the estuary forms one set of clusters, while the stations of the northern zone formed the other clusters.

Month wise water quality parameters of the Cochin estuary formed two clusters (Fig. 4.). The southwest monsoon months form a cluster, except June 2009. Post-monsoon period (summer) and pre-monsoon period (northeast monsoon period) form clusters together. Month wise variation of water quality parameters showed similarity in the pre-monsoon and post monsoon period.

Conclusion

According to EU-Crouzet et al., 1999 method (Table 1.), all the stations were classified as bad based on phosphate concentration. Based on the nitrate + nitrite concentration, stations 4 and 9 were rated as bad while the other sites were observed to be of the poor category. So this index pointed to an extreme deterioration of water quality in the estuary.

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