Trophic status and nutrient regime of Cochin estuarine system, India

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The Cochin estuarine system (CES) being one among the world’s highly polluted and productive estuarine system was monitored to assess the trophic condition in view of the changing nutrient regime. The estuarine system was shallow, with mixo-oligo to mixo-mesohaline salinities (9.65 ± 6.99 ‰). The dissolved oxygen and the pH regime of the water column were 5.92 ± 1.13 mg L-1 and 7.42 ± 0.71, respectively. The study documents high dissolved inorganic nitrogen (28.95 ± 8.47 µmol L-1), dissolved inorganic carbon (1089.87 ± 362.36 µmol L-1), dissolved inorganic phosphate (7.76 ± 3.56 µmol L-1) and gross primary productivity (2.31 ± 1.14 gC m-3 day-1). However, explicitly augmented inorganic nutrients coupled with low dissolved oxygen, pH, and productivity patterns were observed in station 7. High dissolved inorganic carbon denoted net heterotrophic condition. Trophic index (TRIX units) was observed to be high compared to earlier reports, indicated eutrophicated condition with the highest value at station 1 (8.04 ± 0.28). Therefore, proper management interventions are required to restrict allochthonous nutrient loading to protect CES from further anthropogenic impacts and to mitigate the eutrophication process.

Keywords: Anthropogenic, Carbon, Nutrient, Productivity

Introduction

Estuaries represent an interface between marine and freshwater environments. These are the ecosystems where excess nutrients from natural and anthropogenic sources get accrued and thereby characterized by highest rates of biodiversity and biological production. The increasing nutrient concentration has led to enhanced eutrophication rates and oxygen depletion in estuaries worldwide, despite they exchange material and energy with open sea. Estuarine eutrophication has several adverse effects, including a prolific increase of algal blooms, creating hypoxic and even anoxic conditions, substantial loss of biodiversity and habitat, and also may lead to the pollution or impairment of commercial shellfish stocks. In recent decades, most of the Indian estuaries are exposed to alarming rates of anthropogenic interactions due to the rapid increase in the human populace and extensive urbanization. This has accelerated the degree of estuarine degradation, land reclamation, exploitation of fishery resources, leading to augmented aquaculture, agricultural and industrial practices, and accelerated the release of domestic, sewage and industrial discharges which amplified the autochthonous and allochthonous nutrient loading and eutrophification in these systems, causing irrevocable damage to estuarine processes, altering its ecological and economic benefits.

The Cochin estuarine system (CES) is a part of noted Ramsar site - Vembanad Lake, which has drawn attention due to its richness in terms of biodiversity and biological production. The fishery resources form the inevitable part of the everyday diet of neighbouring human settlements and are the main source of income for the local community. The CES is regarded as one of the world’s most polluted estuaries that undergo acute pollution and anthropogenic interventions for the past few decades. The estuarine system receives approximately 104×103 m3 of industrial and 260 m3 of domestic wastes every day, most of which are unprocessed. This is likely to affect the nutrient regime and its dynamics which in turn may alter the productivity patterns and ultimately the fishery potential. Therefore, assessing the trophic status and nutrient dynamics between short interim of time gaps is very much essential for the scientific evaluation of the health and degree of pollution in the CES. These observations could also support us to foresee the reaction of coastal ecosystems to the continuing anthropogenic
interventions. Several indices are available to assess the trophic status, quality, and anthropogenic pressures/ inherent threats of aquatic ecosystems. Though, misuse of the limnological expressions to marine waters is likely to happen, generating uncertainties and complications to convey the findings

In view of this, the current study portrays the trophic state of the CES using TRIX which is the best tool to evaluate the trophic state of coastal marine waters. There are data sets available on the trophic status and nutrient regime of the CES and other parts of Vembnad Lake. However, CES being the hotspot of pollution needs to be critically reassessed with time and space. Moreover, most studies available on the trophic status of the CES have critically looked into the lower estuary. Therefore, our updated knowledge on the trophic status, productivity patterns, nutrient regime, and the physico-chemical variability is very essential for future management plans in the CES, especially in the changing global climate scenario.

Materials and Methods

Study area

The Cochin estuarine system with its associated mangrove patches is the northern extension of Vembnad Lake (9°40′ and 10°12′ N and 76°10′ and 76°30′ E), which is a noted Ramsar site parallel to the south-western coast of India. The estuarine system is nourished by the six rivers - Achancoil, Manimala, Meenachil, Muvattupuzha, Pamba, and Periyar; receives about 2 x 10^10 m^3 y^-1 of freshwater of which more than 60% is received during monsoon season. The CES is linked to the Arabian Sea through the permanent inlets at Cochin and Azhikode, which enables the estuary to flush out a considerable amount of nutrient and organic matter inputs to adjacent coastal regions. Seven study stations were designated along the estuarine system based on various anthropogenic inputs (Fig. 1). The unique features of the study stations are as follows. St. 1 Thevara is highly influenced by discharges from adjacent human settlements and various fish processing units; St. 2 Thoppumpady, near to fishing harbour, receives a high deposition of waste from fishing activity; the human activities include docking operations, jetty operations, intense boating, and fishing activities. St. 3 Bar mouth, near to Fort Kochi, has close connectivity to the Arabian Sea; St. 4 Bolgatty, has undergone wetland degradation and land reclamation during the past few years due to burgeoning multi power projects; St. 5 Marine Science Jetty is highly influenced by ballast water discharge and oil pollution; St. 6 Chittoor, receives sewage, hospital, local and other domestic discharges and St. 7 Fertilizers and Chemicals Travancore Ltd. (FACT), lies near to the industrial belt, receives discharges from various industries. St. 2 to St. 5 is also highly influenced by extensive and frequent dredging activities for maintaining the channels for the transportation of large passage, cargo, and crude oil ships.

Methodology

The study was carried out during February 2014 to January 2015 on a monthly basis from seven selected stations of the CES. Rainfall data were obtained from the Indian meteorological department. The estuarine depth was measured by sinking a graduated weighted rope till it touched the surface sediments and transparency of the water column was measured using a Secchi disc with a diameter of 20 cm. Water samples were collected in triplicate from 1 meter depth using a Niskin water sampler (General Oceanics; 5 L). A CyberScan PCB 650, Eutech water quality analyser was used to measure the temperature,
pH, and salinity of the water samples. An aliquot of each sample was taken in a glass bottle (60 ml) for the measurement of dissolved oxygen (DO)\textsuperscript{17}. Dissolved inorganic phosphate (DIP), dissolved inorganic silicate (DISi), and dissolved inorganic nitrogen (DIN) such as NO$_3$-N, NO$_2$-N and NH$_4$+ -N were analysed spectrophotometrically within few hours of sample collection\textsuperscript{18}. N: P ratio was calculated to understand the trophic state index of the estuaries\textsuperscript{19}. Water samples were also collected in glass bottles (120 ml) which were fixed with saturated mercuric chloride to arrest microbial activity and kept in ice for the analyses of carbon fractions\textsuperscript{20}. From the samples collected for carbon measurements, an aliquot of each sample (~10 ml) was passed through 25 mm GF/F filter and the filtrates were collected for determining dissolved inorganic carbon (DIC). While the other part of the sample that was not filtered (~10 ml) was used for determining total organic carbon (TOC). The carbon fractions were analysed using a TOC elemental analyser (Multi N/C 2100 S Analytik jena, Germany) by wet combustion method.

The gross (GPP) and net (NPP) primary productivity were assessed by the light and dark bottle method\textsuperscript{17}. The vacuum filtration - acetone extraction method was employed to estimate chlorophyll ‘a’ (chl-$a$) from water samples\textsuperscript{21}. Phytoplankton carbon was calculated by multiplying a factor of 50 to chl-$a$ so as to convert it into equivalent carbon biomass\textsuperscript{22-24}. Trophic index (TRIX) which is an amalgamation of four variables such as chl-$a$, oxygen as absolute (%) deviation from saturation, and nutritional factors such as DIN and DIP was used to appraise the degree of deviation from saturation, and nutritional factors such as chl-$a$ was calculated by multiplying a factor of 50 to chl-$a$.

The TRIX was calculated using the equation, \[ \text{TRIX} = (\log_{10} (\text{Chl}-a \times aD%O \times \text{DIN} \times \text{DIP}) + k) / m, \] where, aD%O = oxygen as absolute (%) deviation from saturation (aD%O = abs[100-% O]), k = 1.5 and m = 12/10 = 1.2. The k and m are scale coefficients, used to fix the lower bounds of the index and the adding of the associated trophic scale, from 0 to 10 TRIX units. The TRIX units allocate an immediate measurement of the trophic state for coastal waters. The TRIX unit > 6 indicates highly productive coastal waters; < 4 is associated with scarcely productive coastal waters, while TRIX unit < 3 is related to the open sea. TRIX results were also compared to the European Environment Agency (EEA) classification for phosphorus (phosphate) and nitrogen (nitrite + nitrate), based on its relative concentrations (\textmu mol L$^{-1}$)\textsuperscript{25}. This classification helps to assess the trophic status of the estuary and suggest nitrogen values < 6.5 - good, 6.5 to 9 - fair, 9 to 16 - Poor, > 16 - bad and phosphate values < 0.5 - Good, 0.5 to 0.7 - Fair, 0.7 to 1.1 - Poor, > 1.1 – bad trophic state.

### Statistical analysis

SPSS v22 (Statistical Programme for Social Sciences v22) was used to perform Pearson’s correlation analyses and the two-way analysis of variance (ANOVA) for the measured parameters. PRIMER v6 (Plymouth Routines in Multivariate Ecological Research v6) was used to carry out the Principal Component Analysis for the various measured parameters\textsuperscript{26}.

### Results

#### Physico-chemical attributes

The annual mean rainfall of Kochi was 286.49 ± 286.44 mm, with maximum rainfall during monsoon (594.03 ± 239.66 mm) and minimum during pre-monsoon (103.03 ± 128.17 mm). The estuary is shallow in nature and the mean depth was 2.82 ± 0.49 m, with maximum depth recorded at St. 3 (3.50 ± 0.34 m). Transparency ranged from 0.38 m to 0.78 m (0.60 ± 0.14 m), with lowest transparency during monsoon. The mean ambient air and water temperature recorded was 27.44 ± 0.86 °C and 28.03 ± 0.80 °C, respectively throughout the study. Table 1 displays the mean seasonal disparity of selected parameters spotted during the study. The salinity of the estuary ranged from 1.45 to 29.7 % (9.65 ± 6.99 %), with the lowest salinity ranges in St. 7 and highest in St. 3 (Fig. 2). ANOVA results suggest a significant variation in the salinity ranges between stations (\(f = 15.405, \rho < 0.001\)) of the CES. The mean pH in the water column was 7.42 ± 0.71, with the lowest ranges at St. 7 (4.28 to 6.73). The pH of the estuary slightly dropped during monsoon compared to the rest of the seasons (Fig. 2). ANOVA results suggest a significant variation in the pH between seasons (\(f = 3.93, \rho < 0.001\)) and between stations (\(f = 84.47, \rho < 0.001\)). The mean DO of the estuary was 5.92 ± 1.13 mg L$^{-1}$ with the lowest value at St. 7 (4.50 ± 1.40 mg L$^{-1}$; Fig. 2). A significant variation in DO was observed between seasons (\(f = 13.398, \rho < 0.001\)).

#### Nutrient regime

During the study period, the mean DIN recorded was 28.95 ± 8.47 \textmu mol L$^{-1}$ (Fig. 2), with lowest values during pre-monsoon and highest during the
monsoon season. Regardless of the stations and seasons, DIN was observed high throughout the study period with exponentially high concentrations at St. 7 (41.40 ± 8.32 µmol L⁻¹). NO₃-N (17.68 ± 6.21 µmol L⁻¹) contributed the major part of DIN followed by NH₄⁺-N (10.16 ± 5.65 µmol L⁻¹) and the mean NO₂-N observed was 1.11 ± 0.47 µmol L⁻¹ during the study period. NO₂-N + NO₃-N ranged from 6.69 to 33.84 µmol L⁻¹. A significant variation in NH₄⁺-N, NO₂-N, NO₃-N, and DIN was observed on spatio-temporal basis, with ρ < 0.001. The mean DIP and DISi recorded was 6.86 ± 3.45 µmol L⁻¹ and 31.47 ± 15.57 µmol L⁻¹, respectively and was observed minimum during post-monsoon and maximum during monsoon season (Fig. 2). A significant variation in ANOVA results was observed for DIP between seasons (f = 63.91) and stations (f = 8.21), with ρ < 0.001. Dissolved inorganic silicate showed significant variation in ANOVA results between stations (f = 7.023) and seasons (f = 35.31), with ρ < 0.05. N: P ratio ranged from 1.60 (St. 1 in the month of February) to 9.67 (St. 4 in the month of October) during the present study. N: P ratio was observed highest in St. 5 (7.85 ± 8.10) and lowest in St. 1 (3.49 ± 1.70). The mean TOC in the water column was 272.98 ± 132.82 µmol L⁻¹, with the lowest value recorded in St. 1 (89.13 µmol L⁻¹) and highest in St. 7 (700.34 µmol L⁻¹; Fig. 3). The mean DIC observed during the study was 1305.68 ± 383.58 µmol L⁻¹ with highest value observed in St. 7 (1849.17 µmol L⁻¹) and lowest in St. 3 (495.13 µmol L⁻¹; Fig. 3) and on temporal basis, high DIC was observed during pre-monsoon season. A significant positive correlation was observed when TOC was related to DIC (r = 0.549, ρ = 0.01).

Productivity patterns
The mean GPP and NPP observed during the study period were 2.31 ± 1.14 g C m⁻³ day⁻¹ and 1.20 ± 0.73 g C m⁻³ day⁻¹, respectively. GPP (Fig. 3) and NPP (Fig. 3) were recorded lowest in St. 7 (0.40 g C m⁻³ day⁻¹ and 0.25 g C m⁻³ day⁻¹, respectively) and highest in St. 4 (4.32 g C m⁻³ day⁻¹ and 3.27 g C m⁻³ day⁻¹, respectively). A strong positive correlation was observed when GPP was related to DO (r = 0.517, ρ = 0.000). The mean chl-a observed in the water column was 13.20 ± 7.61 mg m⁻³, with the highest value observed in St. 1 (40.17 mg m⁻³) and lowest in St. 7 (2.82 mg m⁻³; Fig. 3). The mean phytoplankton carbon observed was 654.09 ± 386.39 mg C m⁻³, with a highest value at St. 1 (2008.5 mg C m⁻³) and lowest in St. 7 (141.23 mg C m⁻³). NPP: GPP ratio of the CES ranged from 0.19 to 1.08 during the study period, where most of the values were below 0.5.

Trophic status
TRIX evaluation of the CES revealed a high trophic index irrespective of seasons and stations. The TRIX units ranged from 5.32 (St. 5 in the month of December) to 8.15 (St. 6 in the month of June).
Fig. 2 — Spatio-temporal variation in salinity, pH, DO, DIN, DIP and DISi of the CES during 2014 - 2015

Fig. 3 — Spatio-temporal variation in TOC, DIC, GPP, NPP, Chl-a and TRIX of the CES during 2014 - 2015
Spatially, TRIX was observed lowest in St. 3 (6.91 ± 0.24), while the highest values were recorded at St. 6 (7.89 ± 0.27), followed by St. 1 (7.78 ± 0.15). On seasonal basis, TRIX was observed highest during monsoon season (7.65 ± 0.39) and lowest during the post-monsoon season (7.17 ± 0.55). During pre-monsoon, TRIX was observed highest in St. 6 followed by St. 7; during monsoon highest TRIX units was observed in St. 6, followed by St. 4 and during post-monsoon it was highest in St. 1, followed by St. 6 (Fig. 3).

Principal component analysis

The spatio-temporal variability in environmental parameters was made clear by means of the principal component analysis (PCA) ordination (Fig. 4). In the PCA ordination, the first three principal components assumed for 78.40 % of variability in the environmental conditions for the seven selected study stations. Among this, 63.10 % of environmental variability was based on the first two principal components, with 45.9 % variability on axis 1 (eigenvalue 5.97) and 17.2 % variability on axis 2 (eigenvalue 2.23). Along the axis 1, DIN, GPP, NPP, salinity, DO were observed the most vital determinants of variances between stations, while NH₄⁺-N, NO₂⁻-N, NO₃⁻-N, DIC, TOC were the influencing determinants on axis 2 (Table 2).

Discussion

The spatio-temporal disparities in trophic and nutrient dynamics of the CES were the outcomes of monsoonal discharge and anthropogenic interventions. A scientific knowledge of the variation in environmental parameters, nutrient stoichiometry, and productivity patterns of the CES enables implementation of various management measures that can ensure a progressive reduction in pollution problems, prevent further deterioration, and enables to achieve recovery of the degrading system. Our observations document that the CES remains consistently nutrient-rich, irrespective of seasons, and displayed distinct spatio-temporal variations. Accelerated increase in nutrient loading in estuaries was primarily due to inputs from domestic, sewage and industrial effluents \(^{27}\). During the present study, NO₃⁻-N was the major contributor among DIN, followed by NH₄⁺-N. The high concentration of NH₄⁺-N in the CES is likely due to high nitrogen inputs through anthropogenic sources such as industrial and sewage discharges and agricultural runoff. As the DO has not critically fallen to hypoxic and anoxic conditions, the nitrification processes (aerobic oxidation of NH₄⁺-N to NO₂⁻-N and NO₃⁻-N) can likely be the cause for high NO₃⁻-N in the CES\(^{28,29}\).

The DIN was exponentially high in St.7, mostly due to the inputs (partially treated or untreated) from the adjacent industrial zone (particularly from the FACT that manufactures phosphatic and ammonium sulphate fertilizers). Increased DIN in St. 6 could be possibly due to increased sewage discharge from

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adjacent human settlements. However, as St. 6 is located near to St. 7, it is also likely to receive significant inputs from the industrial zone. Along with this, St. 7 and St. 6 receive the highest amount of river water discharge compared to other stations, which may also contribute to nitrogen loading. The DIN was observed lowest in St. 3 which is likely due to the intrusion of seawater as this station is in near vicinity to the Fortkochi Bar mouth. The greater utilization of DIN due to improved primary production could add to the reason for low DIN during post-monsoon and pre-monsoon. DIP was observed highest in St. 7 where the riverine and industrial discharge were highest compared to the rest of the stations. The present study also suggests that high DIP in the CES were not only due to the contribution from river Periyar but also due to various anthropogenic inputs including industrial discharges (chiefly from FACT). A previous study in the CES also report that the N: P ratios (6.8 to 262) were irregular due to the uneven ammonia inputs from the river Periyar. However, low N: P ratios (1.60 to 9.67) were observed during the present study, due to exponentially high phosphate concentration in the water column. Similar observations were made in Vembanad backwaters. Increased runoff during monsoon has contributed to high DIsi concentrations in the CES. This is likely to favour diatom growth in estuarine environments, particularly during high saline conditions.

The carbon fractions were observed high compared to the earlier report, with the highest ranges spotted during pre-monsoon season. As estuary receives organic matter inputs from various anthropogenic sources, high TOC was observed in all the stations irrespective of seasons. This also indicates that riverine inputs were not the major contributor to carbon in the estuarine system. Studies on carbon dynamics in CES also suggest that the organic carbon load in the estuarine system appears to be anthropogenic in origin. Several studies also point out that indiscriminate discharge of agricultural, aquaculture, industrial, urban, and sewage discharges has significantly contributed to organic enhancement in the estuary. The high DIC observed during the study indicates high rates of organic respiration/decomposition and net heterotrophic conditions in the CES. Riverine inputs, surface runoff, groundwater inflow, and calcite dissolution could also contribute to DIC. High DIC is an indicator of the high CO₂ concentration in the estuary. Studies on carbon dynamics in CES also indicates that the estuary act as an important source of atmospheric CO₂. High DIC can also be a reason for slightly lowered pH profiles compared to earlier report owing to the formation of more hydrogen ions. However, in the CES variation in pH was limited due to the extensive buffering capacity of the seawater. The lowered pH observed in St. 7 is likely due to the influence of industrial discharges.

The high nutrient and organic carbon observed in the CES has likely affected the DO of the estuary. Slightly low DO observed during pre-monsoon season can also be the result of the upwelled circulation of high saline waters and its improved resident time and also may be due to less solubility of gases at increased salinity and temperature. Despite the low salinity ranges, DO was observed low in St. 7, particularly due to the influence of industrial discharges. This can likely be a cause for fish kills observed in CES during the study period. Salinity was mixo-oligohaline to mixo-mesohaline ranges, clearly demarcate the stations spatially and seasonally. The salinity gradient of the CES also favours diverse flora and fauna. The estuarine depth has slightly reduced compared to the latest report. The low depth profiles of the estuary also favour easy mixing of the sediment due to tidal/wave action, facilitating release of nutrients from the sediment to the water column, and thereby affecting estuarine transparency.

The high nutrient concentration supported better productivity patterns in the CES. However, during the present study significantly high nutrient concentration coincided with low primary production (GPP, NPP, and chl-α), DO and pH profiles in the St. The CES act as a matured system exporting substantial amount of nutrients to the adjacent Arabian Sea during monsoon season. This could also add to the reason for slightly lowered nutrient concentration and productivity patterns during pre-monsoon season. The surplus nutrient availability in the CES favoured fairly high chlorophyll ‘a’. However, productivity patterns were not always observed proportional to the chlorophyll ‘a’. High productivity patterns observed during the study could also add to the carbon load in the estuary. The PCA ordination of the CES revealed that DO, salinity, NH4+-N, NO3-N, DIsi, DIC, TOC, and DIP significantly varied during pre-monsoon than monsoon and post-monsoon season. Heavy rainfall
and further runoff have accelerated the nutrient concentration in the estuary, reducing the estuarine transparency during monsoon season. The study also indicates that the increased release of industrial effluents along with riverine inputs modified the physico-chemical characteristics, nutrient concentration, and productivity patterns in St. 7. The TRIX units of the CES were astonishingly high than the previous report and were even high than other parts of the Vembanad Lake. The TRIX units observed were also high than global ranges for estuaries. The relationship of TRIX units to DIN (\( r = 0.41 \), with \( \rho < 0.01 \)), DIP (\( r = 0.61 \), with \( \rho < 0.01 \)), TOC (\( r = 0.23 \), with \( \rho < 0.05 \)), chl-a (\( r = 0.44 \), with \( \rho < 0.01 \)), salinity (\( r = -0.60 \), with \( \rho < 0.01 \)) and DO (\( r = -0.53 \), with \( \rho < 0.01 \)) (Fig. 5) has been validated using Pearson correlation analysis. This specifies the importance of DIN, DIP, TOC, chl-a, salinity, and DO in determining the water quality and trophic condition of the estuary. The observation derived from the TRIX index was reconfirmed by the low NPP: GPP ratios (below 0.5) of the CES, complementing the unhealthy trophic status of the estuary. As per EEA classification the trophic condition of the CES was mostly poor to bad with few exceptions. Therefore, the present study confirms the high pollution rates in the CES, specifies a situation where eutrophication is of great concern, and proper management interventions are required at the earliest.

**Conclusion**

Increasing anthropogenic perturbations have drastically modified the inorganic nutrient and organic carbon concentration in the CES, affecting its physico-chemical characteristics and productivity patterns. In St. 7, high nutrient concentration coincided with low primary production, DO and pH profiles, despite high nutrient concentration and productivity patterns of the CES. High DIC in the CES is likely due to high rates of respiration/OM degradation; indicates net heterotrophic conditions. TRIX units were observed high than the reports from other estuaries globally, indicating the unhealthy status of the CES due to accelerated pollution and enhanced eutrophication. The observations derived from TRIX were comparable to other trophic indices used in the present study. The study recommends that it is vital to adopt remedial measures to prevent further worsening of the estuarine condition and to recover the viability and health of the CES.
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Conflict of Interest

The authors declare no competing or conflict of interest.

Author Contributions

Study design: SBN; Field work and sample analysis: RHN and NVK; Data analysis and Manuscript preparation: RHN; Manuscript revision: SBN and RHN.

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