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ORIGINAL RESEARCH ARTICLE

Seasonal carbonate system *vis-à-vis* pH and Salinity in selected tropical estuaries: Implications on polychaete diversity and composition towards predicting ecological health

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Abstract Salinity and pH play a fundamental role in structuring spatial patterns of physical properties, biota, and biogeochemical processes in the estuarine ecosystem. In this study, the influence of salinity-pH gradient and carbonate system on polychaete diversity in Ennore, Uppanar, Vellar, and Kaduvaiyar estuaries was investigated. Water and sediment samples were collected from September 2017 to August 2018. Univariate and multivariate statistical analyses were employed to define ecological status. Temperature, salinity, pH, and partial pressure of carbon-di-oxide varied between 21 and 30°C; 29 and 39 ppt; 7.4 and 8.3; and 89.216 and 1702.558 μatm, respectively. PCA and CCA results revealed that DO, chlorophyll, carbonate species, and sediment TOC have a higher influence on polychaete community structure. Forty-two species such as *Ancistrosyllis parva*, *Cossura coasta*, *Eunice pennata*, *Euclymene annandalei*, *Lumbrineris albidentata*, *Capitella capitata*, *Prionospio cirrifera*, *P. pinnata*, *P. cirrobranchiata*, and *Notomastus* sp. were found dominantly in all estuaries. Shannon index values ranged between 1.619 (UE-1) and 3.376 (VE-2). Based on these findings, high levels of carbonate species and low pH have a greater impact on polychaete diversity and richness val-

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ues. The results of the AMBI Index revealed that stations UE-1, UE-2, UE-3 in Uppanar, EC-1, EC-2 in Ennore indicate “moderately disturbed”, while other stations are under the “slightly disturbed” category. This trend was quite evident in M-AMBI as well.

1. Introduction

Estuaries are dynamic ecosystems that host one of the highest biodiversity and biological production in the world (Bianchi, 2007). They have been increasingly vulnerable to anthropogenic inputs in recent decades, undergoing complex biogeochemical and hydrological processes. They are vulnerable aquatic ecosystems due to the constant influx of contaminants, mostly from land runoff, agricultural and industrial discharges (Fiorino et al., 2018; Plhalova et al., 2018). Among the environmental parameters prevailing in estuaries, salinity is known to be one of the most important key environmental parameters that control the biological components of the estuarine and marine ecosystems. Equally, changes in water pH mainly depend on CO_2 fluxes through photosynthesis, bicarbonate decomposition, freshwater influx, salinity, and temperature, as well as organic matter degradation (Rajasegar et al., 2002). pH fluctuation may also have negative impacts on the metabolism and growth rate of marine organisms (Guinotte and Fabry, 2008). Furthermore, temperature, salinity, and pH in tandem are known to affect seawater chemistry directly, as well as buffering capacity and elevated CO_2 in estuarine systems (Dickinson et al., 2012; Lannig et al., 2010; Nikinmaa, 2013). It is also reported that the uncharacteristic changes in temperature, pH, and salinity exacerbate adverse effects on biota distribution, mostly on benthic organisms (Bochert et al., 1996; Dean, 2008).

Understandably, estuaries play a key role in the global carbon (C) cycle and carbon dioxide (CO_2) budget (Le Quéré et al., 2016; Regnier et al., 2013). They are characterized by a dynamic range of carbon dioxide (pCO_2) fluxes, which are sequestered in the terrestrial system by photosynthesis and weathering reactions and transported to the ocean through rivers and estuaries. The high fluctuation of pCO_2 in estuaries reflects similar trends of organic carbon stocks and degradation compared to other coastal environments as exemplified in the levels of dissolved organic carbon (DOC), oxygen saturation level ($\%O_2$), and chlorophyll-*a* (Chl *a*). Furthermore, an increase in pCO_2 concentration in the aquatic environment also reduces the availability of carbonate ions, affecting biological and physicochemical processes significantly (Doney et al., 2009; Frankignoulle et al., 1998). Earlier studies have also reported the negative responses to increased pCO_2 exposure on a variety of endpoints in marine organisms at various physicochemical (acid-base) and biological parameters namely survival, growth rate, and reproduction (Freitas et al., 2016; Rodriguez-Romero et al., 2014a,b).

On the other hand, benthic organisms also play a pivotal role in the functioning of estuaries and coastal environments, through re-mineralization and nutrients churning between sediment and the overlying water column (Ingole et al., 2009; Jayaraj et al., 2007). Polychaetes constitute the most dominant component with high species richness and abundance in the invertebrate communities in aquatic environments besides possessing varying levels of tolerance to environmental stress as they have been known as bio-indicators of environmental quality assessment studies worldwide (Jayaraj et al., 2007; Khan et al., 2014; Papageorgiou et al., 2006; Sigamani et al., 2019). Conversely, anthropogenic disturbances, especially pollutants from industrial clusters and urban discharges located along the coast, may result in deleterious effects on the biotic and abiotic variables of an ecosystem leading to dwindling biodiversity in estuarine and marine environments. Earlier studies have done elsewhere also reported that the estuaries act as a sink for pollutants and become impacted by a wide variety of contaminants (Khan et al., 2014; Natesan et al., 2017; Senthilnathan and Balasubramanian, 1994).

The present study aims to investigate the status of ecosystem variability in relation to salinity-pH and carbonate systems influence on the distribution of polychaetes in four select estuaries viz., (i) Ennore, (ii) Uppanar, (iii) Vellar, and (iv) Kaduvaiyar, Southeast coast of India. Ennore estuary is known for the dumping of fly ash slurry from the nearby Ennore thermal plant, and the disposal of municipal domestic wastes. Similarly, on the northern bank of Uppanar, where clusters of industries are located, discharges including coolant water are finding their way into this ecosystem. Quite on the contrary, Vellar and Kaduvaiyar estuaries are known to receive wastes from anthropogenic activities, sewage disposal, and agricultural run-off.

2. Material and methods

2.1. Study area

Ennore estuary is a backwater that drains the Koratalliyar River. It is located in the north-eastern part of Chennai city, Tamilnadu, India, and is spread over an area of 4 km along the coast of the Bay of Bengal. The southern arm of the creek, fringing the northern areas of the city of Chennai, has well-developed industries, utilities, suburban residential areas, and fishing hamlets. The northern section of the creek or Kosastalaiyar backwater is connected to Lake Pulicate and has two major developments: the north Chennai Thermal Power Plant and Ennore port. Development in the northern area is likely to intensify with a major industrial park being proposed at present, including power utilities, petrochemical industries, and chemical storage units.

The confluence of Gadilam and Paravanar rivers forms the Uppanar estuary at Cuddalore’s old town area and opens

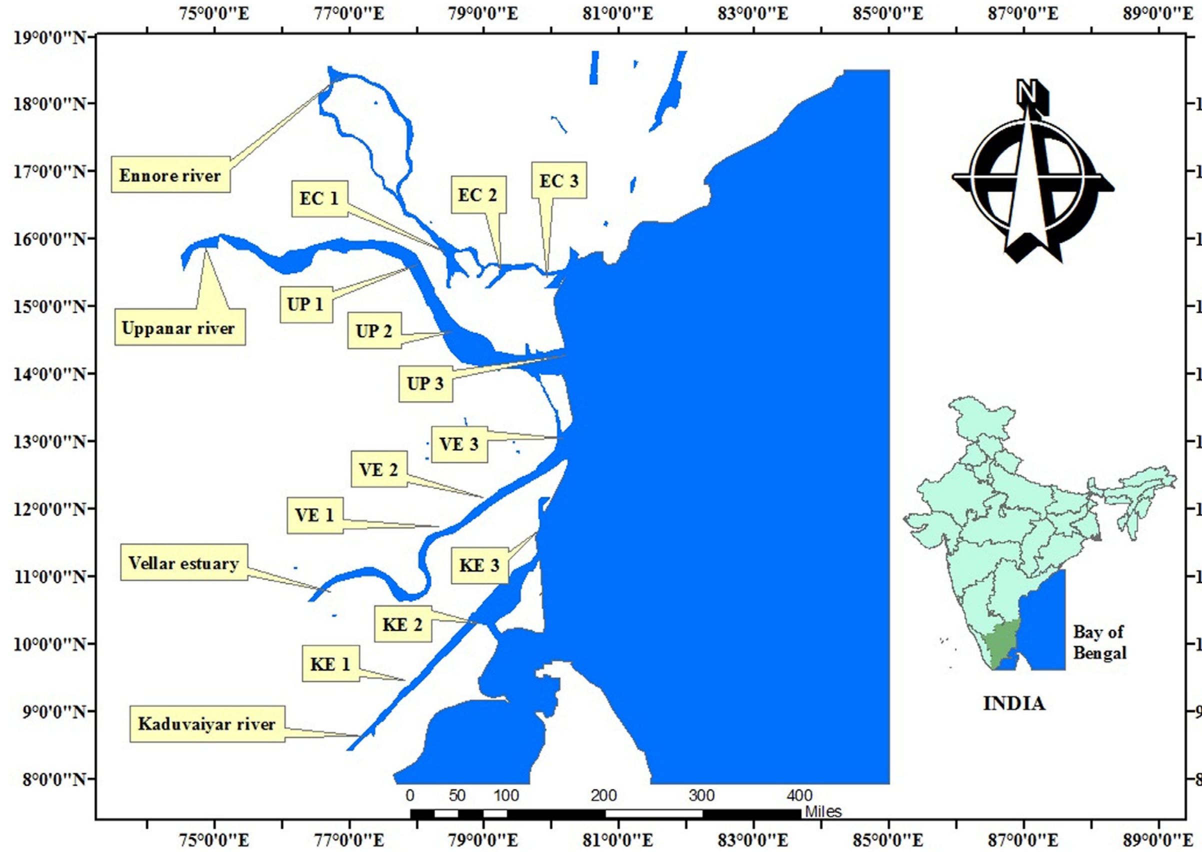

Figure 1 Map showing the sampling stations.

into the Bay of Bengal. The Uppanar estuary is the open type of estuary with the tidal action extending up to a distance of approximately 6 km. The width of the estuary ranges from 20 to 30 m, with an average depth of 2.5 m. It acts as a sink since the large quantity of effluents/discharges accumulated from these industries located on the northern bank of the Uppanar estuary are finding their way into the river.

Contrarily, the Vellar estuary, situated along the southeast coast of India is relatively undisturbed. It presents a semi-diurnal tidal action range from 10—15 km towards the upstream region. The average width and depth of this estuary are 100 m and 2.5 m, respectively, and it receives terrestrial runoff from the river and different channels. The intrusion of neritic water from the sea and freshwater from the land source forms the brackish nature of the Vellar estuary.

The river Kaduviyar is situated near the town Nagapattinam on the east (Coromandel) coast of India. The Kaduviyar estuary has its source in another major river, Cauvery of Tamil Nadu. The Kaduviyar estuary has a year-round connection with the sea and is subjected to semi-diurnal tides with a maximum tidal amplitude of approximately 1.0 m. It flows for a distance of 380 km through an area of red, sandy, leached and laterised black soil in loamy red soil, and finally joins with the Bay of Bengal. A selection of estuaries was made based on their nature and the accrual of discharges from nearby industries and other anthropogenic sources, as well as salinity intrusion; sampling was made accordingly in three stations/locations in each of the following estuaries:

Ennore estuary: EC-1, EC-2, EC-3 (Lat. 13°13′59.19"N, Long. 80°19′1.44"E);

Uppanar estuary: UE-1, UE-2, UE-3 (Lat. 11°42′14.24"N, Long. 79°45′23.89"E);

Vellar estuary: VE-1, VE-2, VE-3 (Lat. 11°29′43.36"N, Long. 79°45′21.42"E) and

Kaduvaiyar estuary: KE-1, KE-2, KE-3 (Lat. 10°45′52.16"N, Long. 79°50′56.95"E) of Southeast coast of India (Figure 1).

2.2. Collection of water and sediment samples

The estuaries are exposed to a microtidal regime, with a tidal range varying between 0.22 m to 1.5 m. The tidal regime is mostly composed of semi-diurnal components. The tidal phase at estuaries is semidiurnal having two peaks and two lows every day. Samples were collected during high tide periods. Water samples were collected using clean plastic 1 L poly-propylene bottles. Parameters such as temperature, pH (Eutech Instrument, Singapore), and salinity (Hand refractometer, Atago co. Ltd., Japan) were recorded in-situ. Dissolved oxygen (DO) and Biological Oxygen Demand (BOD) were measured by following Winkler's titration method (Strickland and Parsons, 1972). To estimate the other physicochemical parameters, water samples were preserved immediately in an icebox and brought to the laboratory in a controlled condition. Total Alkalinity (TA) was quantified in the laboratory by a titrimetric method using methyl orange and phenolphthalein indicators (Gran, 1952); Chlorophyll-*a* concentration was analyzed using Strickland and Parson's method (1972); Dissolved Organic Carbon (DOC) was analyzed using a Shimadzu TOC analyzer (Shimadzu TOC-VCPH); Particulate Organic Carbon (POC) was obtained with GF/F filters (0.45 μm), dried at 65°C and analyzed using an elemental analyzer (Perkin Elmer, 2400), carbonate ion (CO_3), bicarbonate ion (HCO_3), Dissolved Inorganic Carbon (DIC) and carbon-dioxide partial pressure of (pCO_2) were calculated from pH, temperature, salinity and measured using 'Seacarb' package available in 'R' software (Gattuso et al., 2019). The Venice System method was used for the classification of salinity zones (with slight modifications for the requirements of the present study) (Anonymous, 1959). Accordingly, the salinity zones viz., polyhaline (25—30), and euhaline (30—40) were classified. Based on this, stations in various estuaries were categorized.

Sediment samples were collected using a stainless grab sampler. After collection, the sediment samples were shade dried and then homogenized using a mortar and pestle. A known quantity of homogenized samples was subjected to sediment texture using the pipette method of Krumbein and Pettijohn (1938) and Total Organic Carbon (TOC) was calculated with the chromic acid oxidation method (El Wakeel and Riley, 1957).

2.3. Benthic samples

For faunal analysis, sediment samples were collected using a long-armed Peterson Grab, which covered an area of 0.1 m^2. In each station, three replicate samples were collected and then passed through sieves of 0.5 mm. Retained organisms were stored in a clean plastic container and were fixed immediately with 5% formalin to which Rose Bengal (0.1 g/100 ml distilled water) dye was added for easy spotting at the time of sorting. After sorting, the polychaetes were counted and identified to species level by consulting standard references (Day, 1967; Fauvel, 1953).

2.4. Diversity indices and benthic ecological assessment tools

Polychaete data were subjected to the following diversity descriptors i) Shannon index (H') (Shannon and Weaver, 1949), Margalef richness (Margalef, 1958), and Pielou's evenness (Pielou, 1966) using PRIMER software (version 7.0). In addition to diversity indices, ecological health indices namely AMBI (AZTI Marine Biotic Index) and M-AMBI (Multivariate-AZTI Marine Biotic Index) were also adopted by following the method proposed by Borja et al. (2000, 2008); Muxika et al. (2007); AZTI Laboratory (http://ambi.azti.es). To perform AMBI indices, benthic species were assigned to the following five ecological groups based on their sensitivity to the pollutants:

i Ecological Group I (EG-1) — very sensitive to organic enrichment,
ii Ecological Group II (EG-II) — indifferent to organic enrichment,
iii Ecological Group III (EG-III) — tolerant to excess organic enrichment,
iv Ecological Group IV (EG-IV) — second-order opportunistic species and
v Ecological Group V (EG-V) — first-order opportunistic species.

Borja et al. (2000) further categorized the following classifications with their scale ranges based on the above-mentioned ecological groups as unpolluted (0.0—1.0); slightly polluted (1.1—2.0); moderately polluted (2.1—4.0); heavily polluted (4.1—6.0) and extremely polluted (6.1—7.0). Accordingly, the distribution of these ecological groups were further analyzed according to their sensitivity to pollution stress using BI (Biotic Index) with eight levels (0—7) (Hily et al., 1986; Majeed, 1987). To confirm the trend of AMBI, the M-AMBI index was also calculated which expresses the relationship between observed values and reference condition values. At high quality status, the M-AMBI approaches 1 and at bad quality status, it approaches 0. The threshold values are as follows: high quality > 0.80, good quality 0.57—0.80, moderate quality 0.38—0.57, and bad quality < 0.20 (Muxika et al. 2007). These reference values were accomplished with the WFD requirements.

2.5. Statistical treatment for environmental parameters

Variations in physicochemical parameters are shown in a scatterplot. One-way ANOVA was performed using Tukey's test to observe the variation among the stations. To ascertain the relationship among the environmental parameters, a PCA biplot was drawn using physicochemical parameters *vs* seasons. Canonical Correspondence Analysis (CCA) was drawn to determine the relationship between environmental parameters and polychaetes. All the above-stated graphical and various multivariate analyses were performed using the statistical language R version 3.5 (R Development Core Team, 2018). Scatterplot and PCA biplot was plotted using "ggplot2" of 'R' software (Wickham et al., 2018). The CCA was used to run "Vegan 2.4.4" of 'R' software (Oksanen et al., 2017).

3. Results

3.1. Physico-chemical characteristics

The mean with SD values of physicochemical parameters recorded at each sampling location is summarized in Supplementary Table 1. The surface water was characterized by a salinity gradient from 26.0 to 39.0 ppt (mean 32.0±3.5, $F = 1.181$, $p < 0.1$) with a maximum during summer (VE-3) and a minimum during monsoon season (KE-1); pH varied between 7.4 (UE-1) and 8.3 (EC-1 & VE-3) (mean 7.9±0.2, $F = 1.691$, $p < 0.1$) showing significant variations and water temperature reaching 30.0°C (EC-2) during summer and a trough of 21.0°C (VE-1) during pre-monsoon, with statistically significant variations (mean 25.4±1.9, $F = 4.058$, $p < 0.05$).

A positive linear relationship was inferred between water temperature versus salinity and pH (Figure 2a). Dissolved oxygen ranged between 3.1 (EC-2, summer) and 4.8 mg/l (UE-1, pre-monsoon), (mean 3.9±0.4, $F = 2.189$,

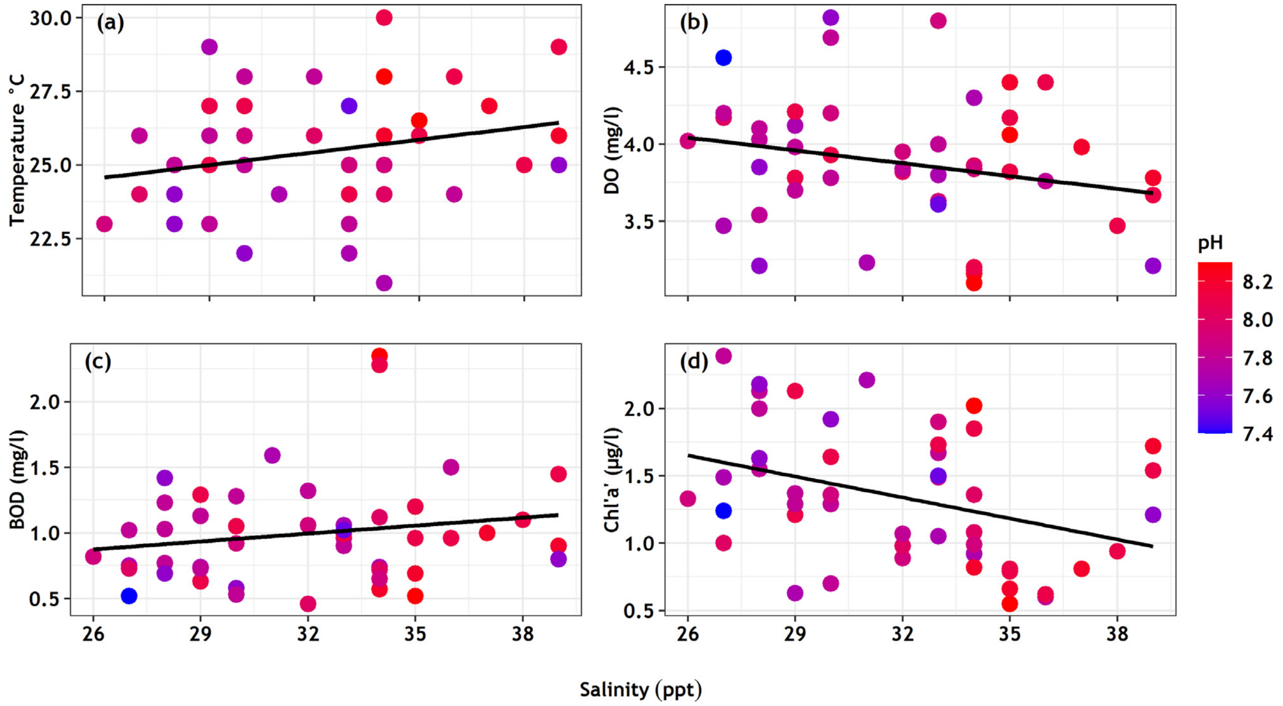

Figure 2 Variation of physico-chemical parameters during the study period; (a) temperature versus salinity-pH, (b) dissolved oxygen (DO) versus salinity-pH, (c) biological oxygen demand (BOD) versus salinity-pH, and (d) chlorophyll versus salinity-pH.

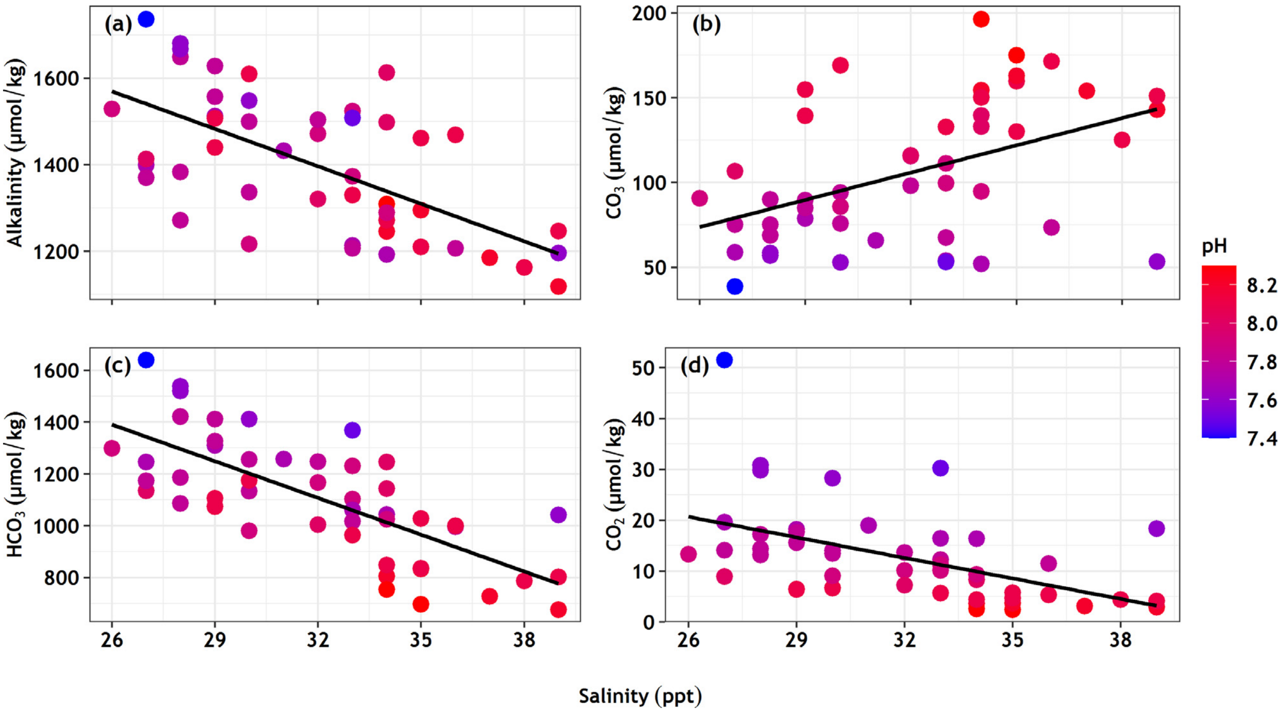

Figure 3 Variation of physico-chemical parameters during the study period; (a) alkalinity versus salinity-pH, (b) carbonate ion versus salinity-pH, (c) bicarbonate ion versus salinity-pH, and (d) carbon dioxide versus salinity-pH.

$p < 0.05$). Unlike temperature, a negative linear relationship was found between DO versus salinity-pH (Figure 2b). The range of BOD was found to vary between 0.5 (UE-1) and 2.4 mg/l (EC-2) with lower values during the monsoon season and high values during the summer season (mean 1.0±0.4, $F = 3.515$, $p < 0.05$). Biological oxygen demand versus salinity and pH showed a positive linear relationship (Figure 2c). Chlorophyll-*a* concentration exhibited high values (2.4 µg/l) at VE-1 during the monsoon season and lower values (0.6 µg/l) at KE-3 during summer season. A negative linear relationship was found between chlorophyll-*a* and salinity-pH (Figure 2d).

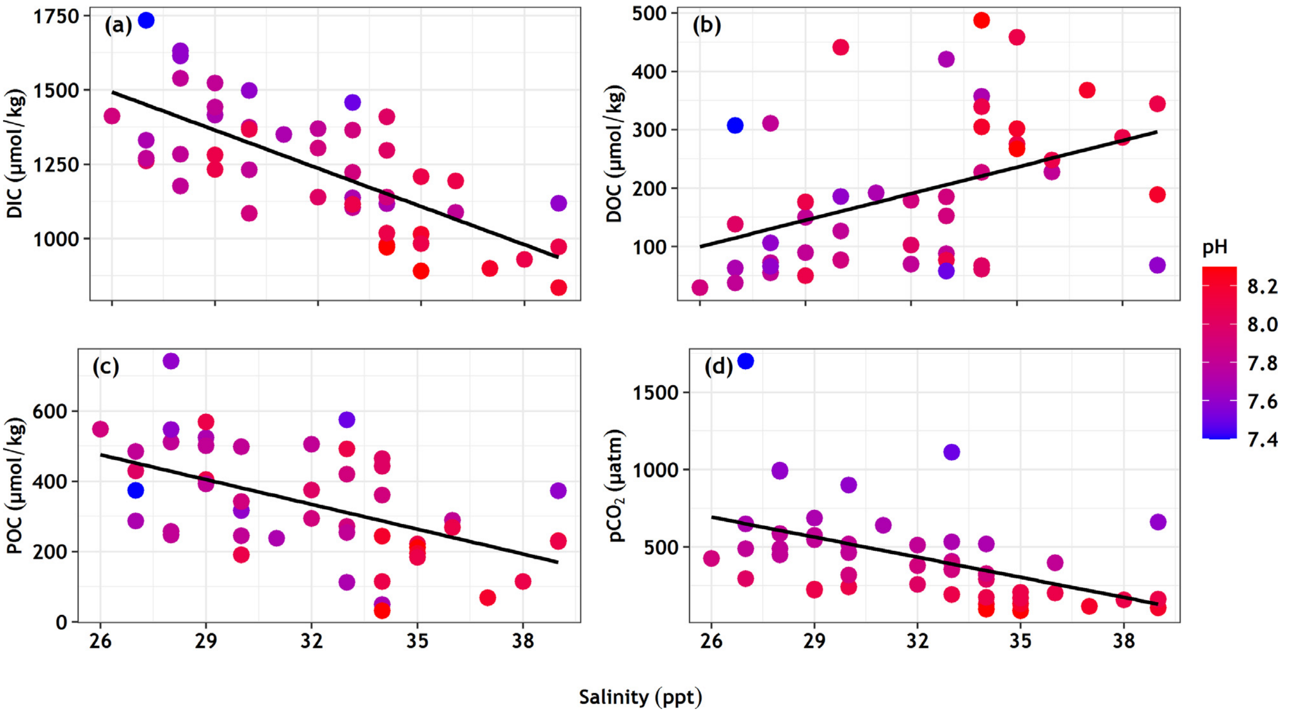

Figure 4 Variation of physico-chemical parameters during the study period; (a) dissolved inorganic carbon (DIC) versus salinity-pH, (b) dissolved organic carbon (DOC) versus salinity-pH, (c) particulate organic carbon (POC) versus salinity-pH, and (d) partial pressure of CO$_2$ (pCO$_2$) versus salinity-pH.

Further, total alkalinity varied from 1118.9 (VE-3) to 1736.4 μmol/kg (UE-1) with significant variations among stations (mean 1396.4±160.6, $F = 7.747$, $p < 0.001$). For total alkalinity, salinity and pH, a negative linear relationship was observed (Figure 3a). Carbonate ion and bicarbonate ion values exhibited a maximum of 196.3 μmol/kg (EC-1) during summer and a minimum of 38.7 μmol/kg (UE-1) during monsoon season (mean 105.8±41.4, $F = 1.769$, $p < 0.1$) and from 676.2 μmol/kg (VE-3, summer) to 1640.4 μmol/kg (UE-1, monsoon), respectively (mean 1107.2±227.7, $F = 3.031$, $p < 0.05$). For carbonate ions versus salinity — pH gradient, a positive correlation was observed (Figure 3b) while HCO$_3$ showed a negative correlation with salinity and pH (Figure 3c). Similarly, pCO$_2$ showed a wide variation from 2.4 (KE-3) to 51.5 μmol/kg (UE-1) (mean 12.6±9.3, $F = 3.202$, $p < 0.05$) with a negative linear relationship against salinity-pH gradient (Figure 3d).

Dissolved inorganic carbon (DIC) concentrations ranged between 835.8 (VE-3) and 1734.3 μmol/kg (UE-1) with a non-conservative decreasing trend along the salinity-pH gradient (Figure 4a) during the summer season whereas increasing trend during the monsoon season (mean 1236.2±207.9, $F = 3.965$, $p < 0.001$). Dissolved organic carbon concentration ranged from 30.1 (KE-1) to 487.5 μmol/kg (EC-1) (mean 190.4±125.8, $F = 0.864$, $p < 0.1$) with a maximum during summer and a minimum during the monsoon season showing a positive linear relationship along the salinity-pH gradient (Figure 4b). Particulate organic carbon varied greatly between 32.0 (VE-3) and 742.5 μmol/kg (EC-1), with a maximum value recorded during the monsoon season and minimum during summer season (mean 334.3±175.5, $F = 0.936$, $p < 0.1$) and thus a negative linear relationship was observed between POC versus salinity — pH gradient (Figure 4c). pCO$_2$ also varied significantly from 89.2 (KE-3) to 1702.6 μatm (UE-1), with significant variations (mean 434.0±307.1, $F = 3.084$, $p < 0.01$), coupled with a non-conservative decreasing trend along with the salinity — pH gradient (Figure 4d). Similarly, linking pCO$_2$ versus pH, a negative linear relationship emerged (Figure 5). Similarly, an increasing trend was observed with DIC (Figure 6a), POC (Figure 6c), and pCO$_2$ (Figure 6d) along the pH gradient barring DOC wherein a negative linear relationship was found (Figure 6b).

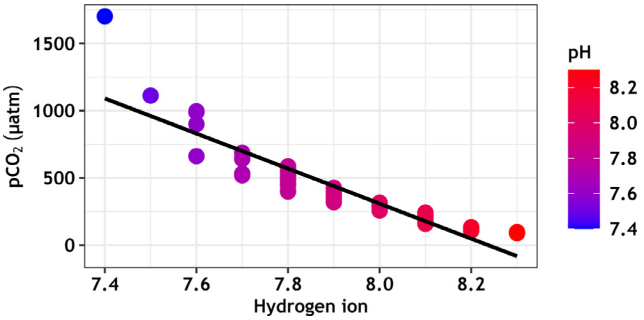

Figure 5 Partial pressure of carbon dioxide versus pH during the study period.

3.2. Sediment characteristics

TOC content ranged between 3.7 (VE-2) and 9.7 mgC/g (EC-1) with a maximum value during the summer and min-

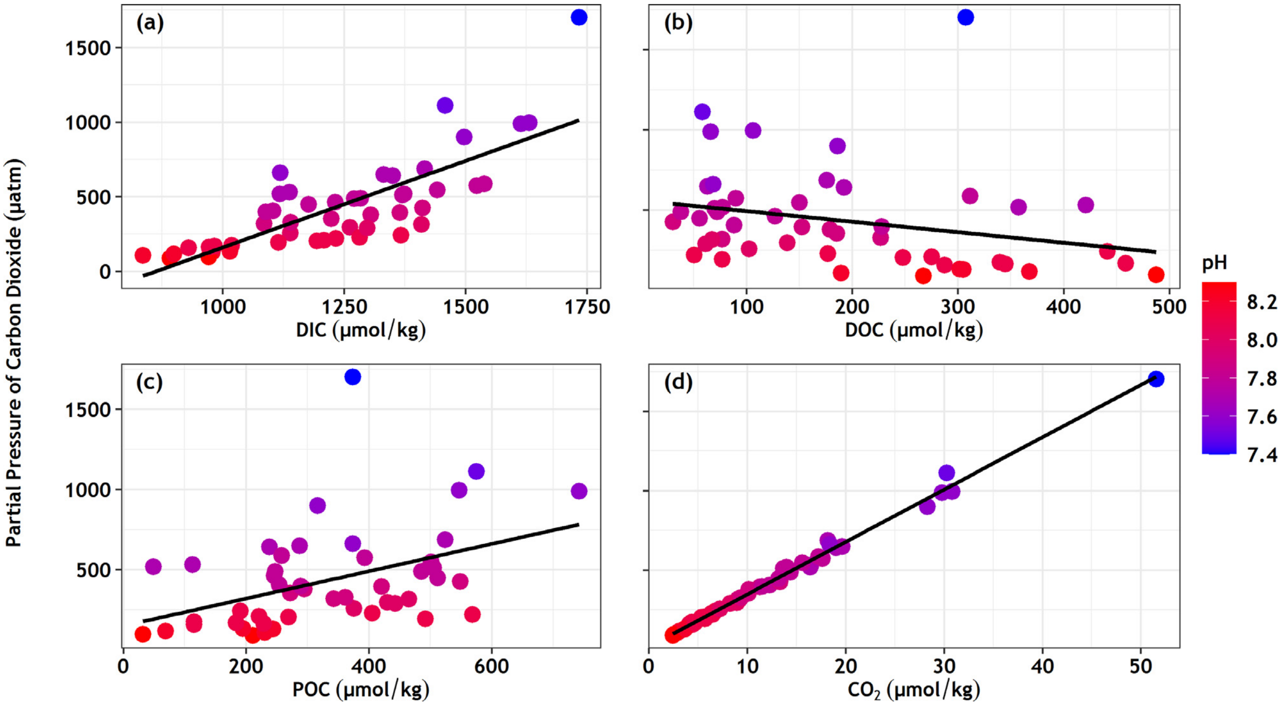

Figure 6 Variation of physico-chemical parameters during the study period; (a) dissolved inorganic carbon (DIC) versus partial pressure of CO_2 (pCO_2), (b) dissolved organic carbon (DOC) versus partial pressure of CO_2 (pCO_2), (c) particulate organic carbon (POC) versus partial pressure of CO_2 (pCO_2), and (d) carbon dioxide versus partial pressure of CO_2 (pCO_2).

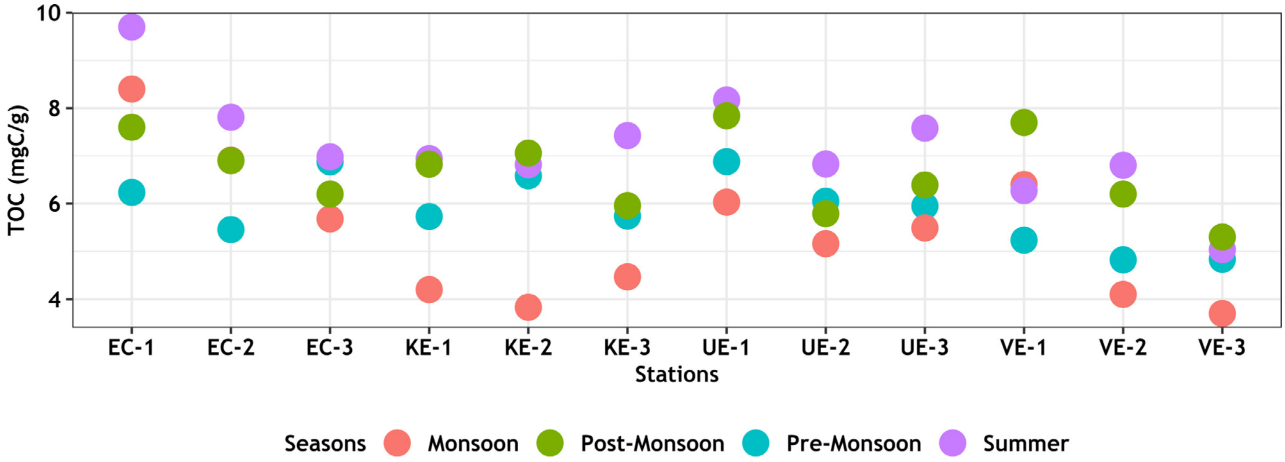

Figure 7 Seasonal variations of sedimentary total organic carbon (TOC) recorded in various stations of the study area.

imum value during the monsoon season (mean 6.3±1.2, $F = 2.301$, $p < 0.05$) (Figure 7). Sediment texture indicated that clay content is relatively high compared to sand and silt. Clay ranged between 4.25 (VE-1, monsoon) and 87.47% (KE-1, summer) followed by sand with a range from 2.37 (UE-1, monsoon) to 56.45% (VE-1, premonsoon) and silt from 5.35 to 49.34% with a peak in VE-3 (monsoon) and a trough in KE-1 (summer) (Figure 8).

3.3. Principal Component Analysis (PCA)

The principal component analysis plot revealed four large groups (Figure 9). Two components explained 55.69% of total variance with 41.54% and 14.15% of components 1 and 2, respectively. The component representing DO, chlorophyll, HCO_3, alkalinity, DIC, POC, pCO_2, CO_2, sediment TOC, and clays point towards pre-monsoon, monsoon, and postmonsoon, while those representing temperature, salinity, pH, BOD, CO_3, DOC, sand, and silt point towards the summer season. PCA plots drawn for individual estuaries are illustrated in Supplementary Figure 1.

3.4. Canonical Correspondence Analysis (CCA)

The canonical correspondence analysis describes the principal tendencies in the relationship between the environmental variables and polychaete assemblage. Components 1 and 2 explained 42.24% of the total variability

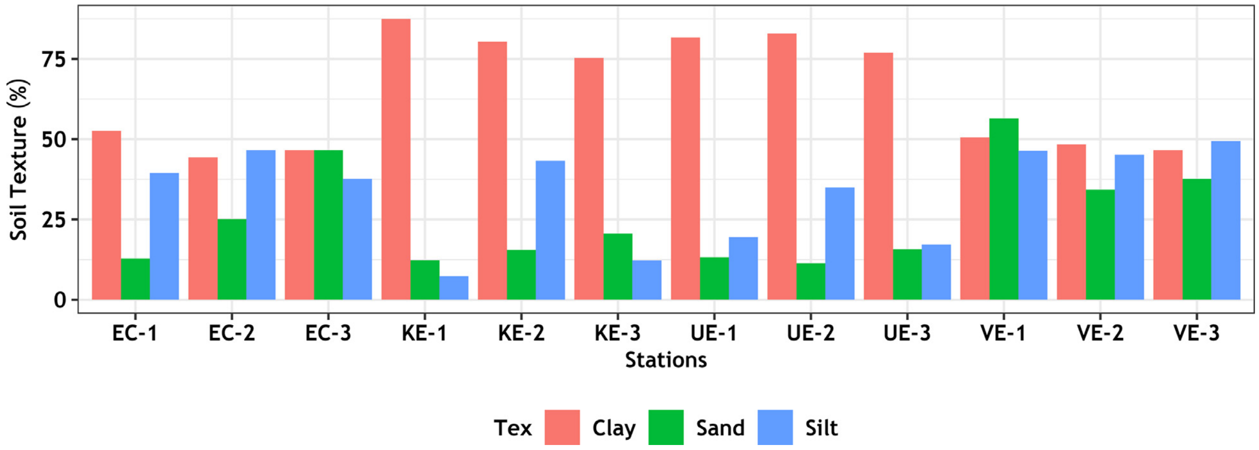

Figure 8 Variations in the sediment texture recorded in various stations of the study area.

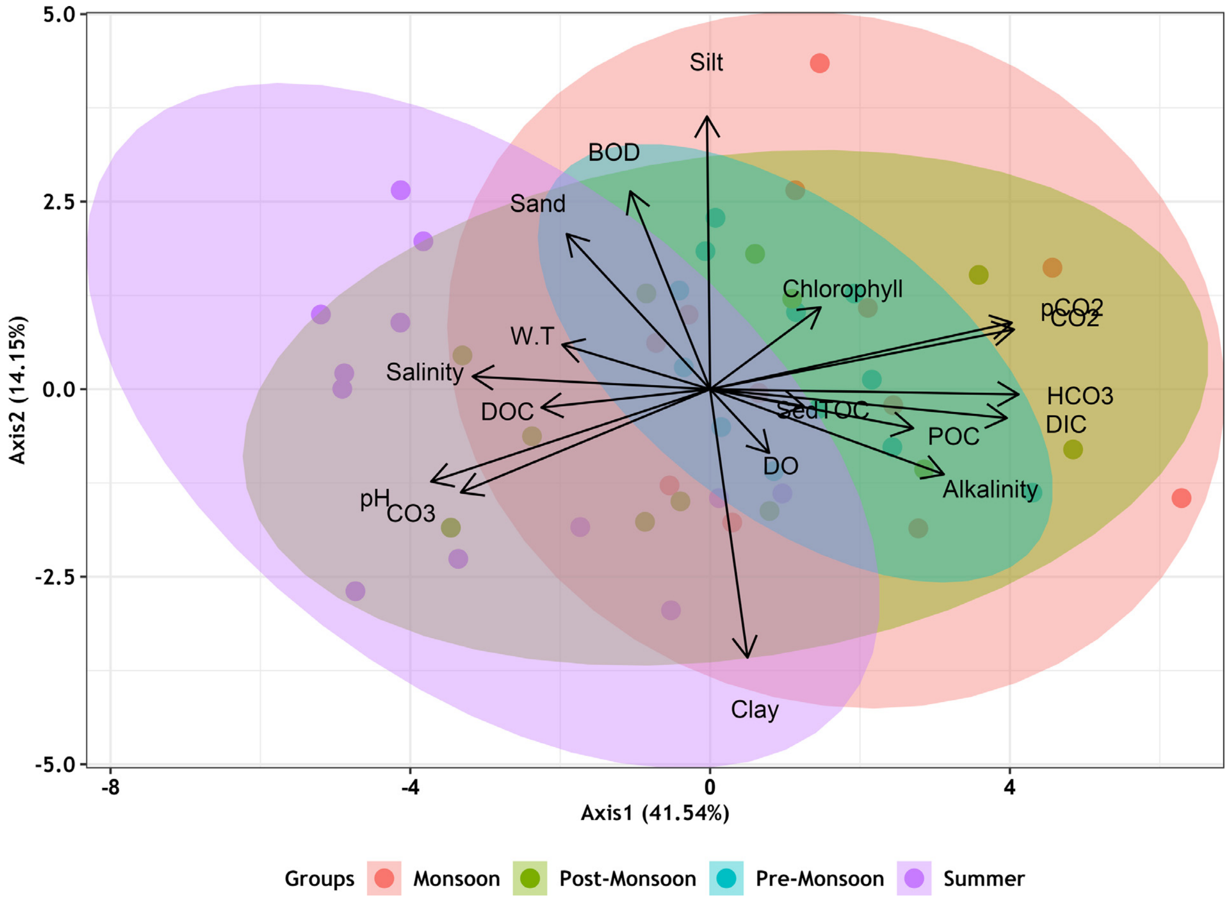

Figure 9 Principal component analysis drawn for the interrelation among environmental parameters and seasons.

of species-environment biplot and accordingly the following environmental parameters such as pH, salinity, DO, CO_3, sand, clay, DOC had a positive correlation in component 1 and polychaetes namely *Cirratulus cirratus*, *Cossura coasta*, *Diopatra cuprea*, *Diopatra neapolitana*, *Dorvillea* sp., *Glycera benguellana*, *Maldane sarsi*, *Marphysa* sp., *Nephtys dibranchis*, *Notomastus aberans*, *Phylo capensis*, *Pista cristata*, *Pygospio elegans*, *Sabella* sp., *Syllis anops*, *Thelepus* sp., emerged as highly correlated species with maximum canonical values (0.5376, 0.4554, 0.2993, 0.2990, 0.2879, 0.2040, 0.1967 and 0.1929) (Figure 10). Contrarily in component 2, temperature, BOD, chlorophyll, alkalinity, HCO_3, DIC, POC, pCO_2, CO_2, Sed.TOC, and silt exhibited a negative correlation with *Ancistrosyllis parva*, *Ancistrosyllis* sp., *Capitella capitata*, *Cirratulus filiformis*, *Euclymene annandalei*, *Eunice pennata*, *Eunice* sp., *Glycera unicornis*, *Goniada emerita*, *Goniada* sp., *Lumbrineris aberrans*, *Lumbrineris albidentata*, *Nereis diversicolor*, *Nereis* sp., *Notomastus* sp., *Ophelia* sp., *Pectinaria* sp., *Pista quadrilobata*, *Platynereis dumerilii*, *Platynereis* sp., *Poly-*

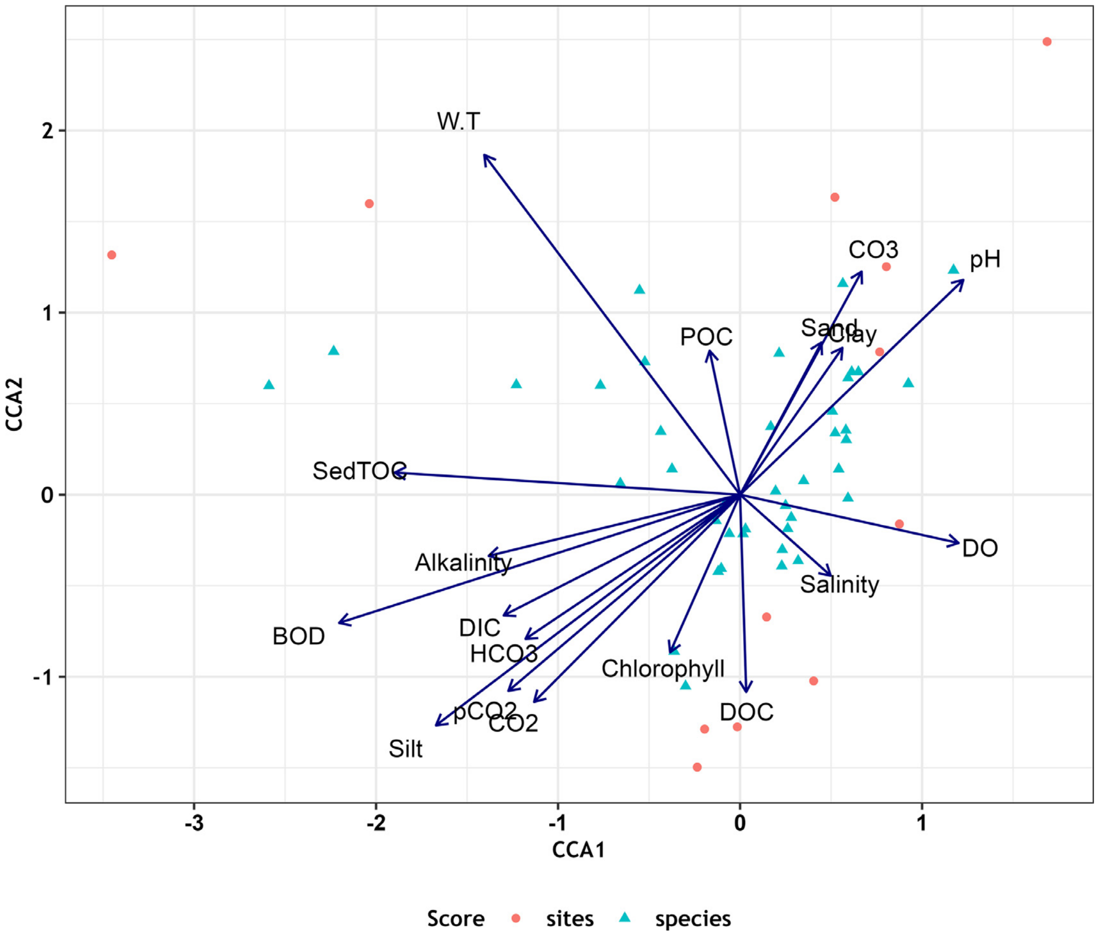

Figure 10 Ordination of polychaete species against environmental variables recorded during the study.

dora capensis, Prionospio cirriferra, P. cirrobranchiata, P. pinnata, Serpula sp. as highly associated polychaete species.

3.5. Biological entities

Polychaete density was found to vary from 518 to 4723 in d m^{-2} with a maximum observed during summer and minimum during monsoon season. Together 42 species of benthic polychaetes were recorded during the study with a maximum species in Vellar estuary (41 species) followed by Kaduvaiyar estuary (31 species), Ennore creek (30 species), and Uppanar estuary (25 species). The most abundant species were *Capitella capitata, Prionospio cirrifera, P. pinnata, P. cirrobranchiata*, and *Notomastus* sp. in Ennore and Uppanar estuaries; *Ancistrosyllis parva, Cossura coasta, Eunice pennata, Euclymene annandalei, Lumbrineris albidentata, Nephtys dibranchis*, and *Pectinaria* sp. in Vellar and Kaduvaiyar.

Similarly, the species *Cirratulus cirratus, Cirratulus filiformis, Cossura coasta, Diopatra cuprea, Diopatra neapolitana, Prionospio cirrifera, Notomastus aberans*, and *Notomastus* sp. was found to be more common in Vellar, Kaduvaiyar, Ennore, and Uppanar; followed by *Ancistrosyllis parva, Euclymene annandalei, Eunice* sp., *Glycera* sp., *Goniada* sp., *Lumbrineris albidentata, Marphysa* sp., *Nephtys dibranchis, Nereis* sp., *Notomastus* sp., *Pista cristata, Platynereis* sp., *Polydora capensis*, and *Pygospio elegans*.

With respect to the salinity gradient zone, as many as 42 polychaete species were observed, with a maximum number of polychaetes recorded in the polyhaline zone (salinity range from 25 to 30 ppt) and minimum number in the Euhaline zone (salinity range from 30 to 40 ppt). Among the polychaete families, representatives from Capitellidae, Eunicidae, Lumbrineridae, Nephtyidae, Nereididae, Spionidae were found to be dominant in the euhaline zone, and those of Cirratulidae, Cossuridae, Dorvilleidae, Glyceridae, Goniadidae, Maldanidae, Onuphidae, Opheliidae, Orbiniidae, Pectinariidae, Pilargidae, Sabellidae, Syllidae, and Terebellidae in the polyhaline zone. Table 2 lists the number of polychaetes recorded in the salinity zones of various estuaries.

3.6. Diversity indices

Species diversity (H') varied from 1.6 (UE-1, monsoon) to 3.4 (VE-2, summer), species richness (d) fluctuated between 3.0 and 6.9 with a maximum in UE-1(summer) and minimum in VE-2 (monsoon). Regarding Pielou's species evenness (J), it ranged between 0.6 and 0.9 with a peak in VE-2 (summer) and a trough in UE-1 (monsoon).

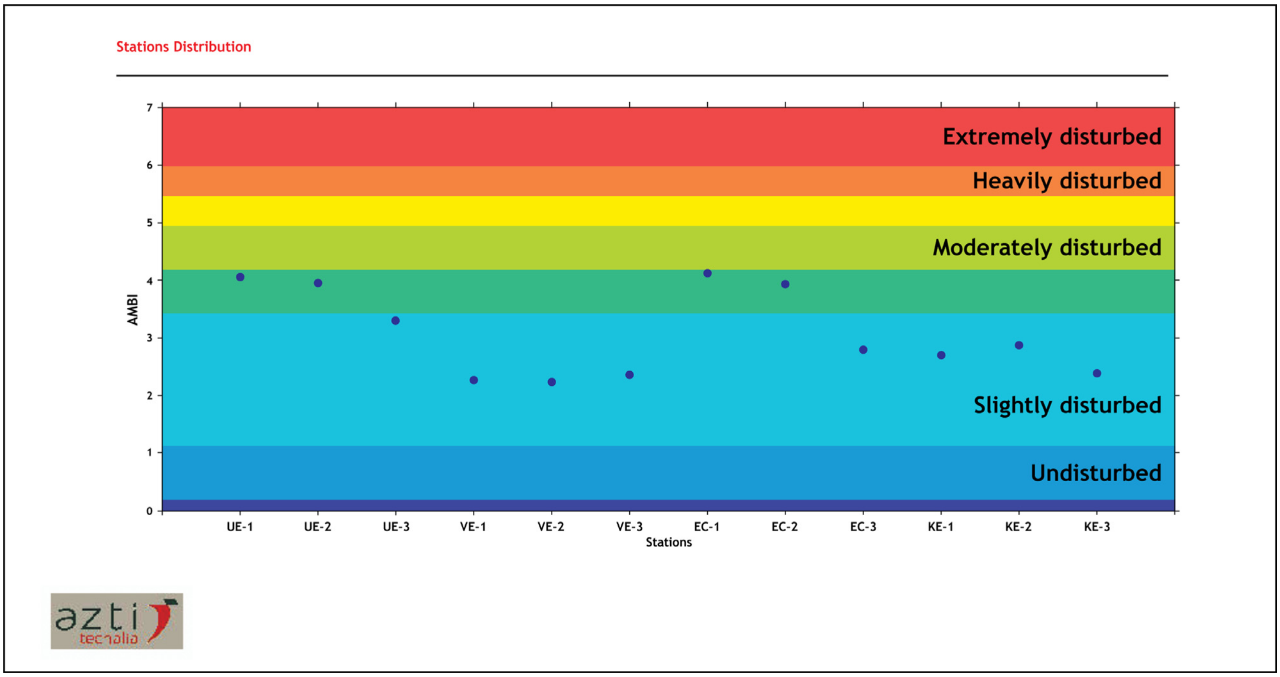

Figure 11 AZTI Marine Biotic Index (AMBI) disturbance classification values in stations of various estuaries during the study.

3.7. Ecological health assessment using biotic indices

The AMBI values calculated for benthic polychaetes fluctuated from 2.23 to 4.12, with a peak at EC-1 and a trough in VE-2 indicated stations UE-1, UE-2, UE-3 in Uppanar; EC-1 and EC-2 in Ennore belong to the category of moderately disturbed; while stations namely VE-1, VE-2, and VE-3 in Vellar, KE-1, KE-2, and KE-3 in Kaduvaiyar and EC-3 in Ennore belonged to the slightly disturbed category (Figure 11). Similarly, M-AMBI values ranged between 0.49 and 0.99 indicating that stations UE-1, UE-2, and EC-1 fell into moderate ecological health status, while other stations into good and high ecological health status (Figure 12, Table 1).

4. Discussion

Estuarine environments are subjected to changes in physicochemical properties due to continuous mixing of freshwater with brackish waters as well as discharges from urban and other sources (Bianchi, 2007). The estimation of water quality is fundamental in determining the health of an ecosystem (Chang, 2008). In the present study, salinity-pH coincided with their variation throughout the study and followed the same pattern with a gradual rise and fall. Among the seasons, a typical upstream-downstream salinity gradient was observed with a minimum of 26.0 ppt (KE-1, monsoon) and a maximum of 39.0 ppt (VE-3, summer). Similarly, water pH showed seasonal variation from 7.4 (UE-1, monsoon) to 8.3 (EC-1 and KE-3, summer). Temperature showed wide variations between 21.0 (VE-1, pre-monsoon) and 30.0°C (EC-2, summer), indicating a positive linear relationship with salinity and pH. High values during summer could be attributed to faster evaporation and low values during the monsoon season due to the dilution of brackish water and freshwater influx in the respective area. The findings of the present study are in close agreement with the trends observed in other studies made elsewhere (Bharathi et al., 2018; Bouillon et al., 2003; Vajravelu et al., 2018).

Dissolved oxygen concentrations ranged between 3.1 (EC-1) and 4.8 mg/l (UE-1) and accordingly a negative linear relationship was observed with salinity and pH. The highest values registered in the pre-monsoon season were attributed to the influx of freshwater. On the contrary, regarding BOD, a maximum value was observed during summer and a minimum level was observed during the monsoon season with a positive correlation to salinity and pH. A similar distribution of DO content with a maximum during the monsoon and minimum during the summer season was reported earlier by Morgan et al. (2006) in Upper Kaskaskia rivers and Sigamani et al. (2015) in Vellar—Coleroon estuarine complex, southeast coast of India.

Conversely, the chlorophyll value exhibited a maximum during the monsoon at VE-1 and a minimum during the summer season at KE-3. The higher value could be due to wind-induced upwelling and river runoff, which would have increased the chlorophyll level. A negative correlation was found between chlorophyll-*a* versus salinity and pH. Chlorophyll concentrations recorded are comparable to those reported in earlier studies (Cloern et al. (2017) in San Francisco Bay and Shanthi et al. (2015) in Bengal Bay).

Total alkalinity is an important factor in determining the estuary's ability to neutralize acidification from rainfall or wastewater. Alkaline compounds such as CO_3, HCO_3, and hydroxides, remove hydrogen ions and thus lower the acidity of the water (Toma, 2013). In the present investigation, the maximum alkalinity was recorded during the monsoon (UE-1) and the minimum (VE-3) during the summer season. There was a negative link between the salinity-pH gradient

Table 1 AMBI, ecological groups, BI-disturbance classification, and M-AMBI status of the stations during the study.

Stations	EG I (%)	EG II (%)	EG III (%)	EG IV (%)	EG V (%)	AMBI	BI from mean AMBI	Disturbance classification	M-AMBI	Status
EC-1	3.093	6.186	11.34	71.649	7.732	4.12	3	Moderately disturbed	0.50	Moderate
EC-2	4.167	8.333	14.583	66.667	6.25	3.94	3	Moderately disturbed	0.59	Good
EC-3	11.864	23.729	42.373	10.169	11.864	2.80	2	Slightly disturbed	0.75	Good
UE-1	1.282	8.333	10.897	77.564	1.923	4.06	3	Moderately disturbed	0.49	Moderate
UE-2	1.961	11.111	13.072	69.281	4.575	3.95	3	Moderately disturbed	0.56	Moderate
UE-3	2.041	14.286	55.102	18.367	10.204	3.31	3	Moderately disturbed	0.64	Good
VE-1	22.581	33.871	19.355	17.742	6.452	2.27	2	Slightly disturbed	0.93	High
VE-2	30.488	20.732	21.951	23.171	3.659	2.23	2	Slightly disturbed	0.98	High
VE-3	20	31.429	25.714	17.143	5.714	2.36	2	Slightly disturbed	0.88	High
KE-1	27.778	8.333	33.333	16.667	13.889	2.71	2	Slightly disturbed	0.70	Good
KE-2	11.111	30.556	19.444	33.333	5.556	2.88	2	Slightly disturbed	0.76	Good
KE-3	26.471	32.353	11.765	14.706	14.706	2.38	2	Slightly disturbed	0.76	Good

AMBI: AZTI marine biotic index; BI: biotic index; M-AMBI: Multivariate-AMBI.

Table 2 Polychaete species recorded in the polyhaline and euhaline zones of the select estuaries (September 2017—August 2018).

Family	Polychaete species	UE (pH 7.4—8.1)		VE (pH 7.6—8.1)		EC (pH 7.5—8.3)		KE (pH 7.7—8.3)	
		Polyhaline Sal (25—30)	Euhaline Sal (30—40)	Polyhaline Sal (25—30)	Euhaline Sal (30—40)	Polyhaline Sal (25—30)	Euhaline Sal (30—40)	Polyhaline Sal (25—30)	Euhaline Sal (30—40)
Capitellidae	*Capitella capitata*	+	-	+	+	+	+	+	+
	Notomastus aberans	+	-	+	-	+	-	+	-
	Notomastus sp.	+	+	+	+	+	+	+	+
Cirratulidae	*Cirratulus cirratus*	+	+	+	+	+	+	+	+
	C. filiformis	-	-	+	-	-	-	+	+
Cossuridae	*Cossura coasta*	-	-	+	+	-	-	-	-
Dorvilleidae	*Dorvillea* sp.	-	-	+	+	+	-	-	-
Eunicidae	*Eunice pennata*	+	+	+	+	+	+	+	+
	Eunice sp.	-	-	+	+	+	+	+	+
	Marphysa sp.	+	+	+	+	+	+	+	-
Glyceridae	*Glycera benguellana*	-	-	+	+	-	-	+	+
	G. unicornis	+	+	+	-	+	+	-	-
Goniadidae	*Goniada emeriti*	+	-	-	-	+	-	-	-
	Goniada sp.	+	+	+	+	+	+	-	-
Lumbrineridae	*Lumbrineris aberrans*	-	-	+	+	-	-	+	-
	L. albidentata	+	+	+	+	+	+	+	+
Maldanidae	*Euclymene annandalei*	-	-	+	+	+	+	+	+
	Maldane sarsi	-	-	+	-	+	-	-	-
Nephtyidae	*Nephtys dibranchis*	+	-	+	+	+	+	+	-
	N. hombergi	+	+	+	+	+	+	+	+
Nereididae	*Nereis diversicolor*	+	-	+	+	+	-	-	-
	Nereis sp.	+	+	+	+	+	+	+	+
	Platynereis dumerilii	+	+	+	+	+	-	-	-
	Platynereis sp.	+	+	+	+	+	+	+	+
Onuphidae	*Diopatra cuprea*	-	-	+	-	-	-	-	-
	D. neapolitana	-	-	+	-	+	-	+	-
Opheliidae	*Ophelia* sp.	-	-	+	+	-	-	+	+
Orbiniidae	*Phylo capensis*	+	+	+	+	-	-	+	+
Pectinariidae	*Pectinaria* sp.	+	+	+	+	+	+	+	+
Pilargidae	*Ancistrosyllis parva*	+	-	+	+	-	-	-	-
	Ancistrosyllis sp.	+	+	+	+	+	+	+	+
Sabellidae	*Sabella* sp.	-	-	+	-	+	-	-	-
	Serpula sp.	-	-	+	-	+	-	-	-
Spionidae	*Polydora capensis*	+	-	+	+	-	-	+	-
	Prionospio cirriferra	+	+	+	+	+	-	+	+
	P. pinnata	+	+	+	+	+	-	+	+
	P. cirrobranchiata	+	+	+	+	+	-	+	+
	Pygospio elegans	+	-	+	+	+	+	-	-
Syllidae	*Syllis anops*	-	-	+	+	+	+	+	+
Terebellidae	*Pista quadrilobata*	-	-	+	-	-	-	+	-
	P. cristata	+	-	+	+	+	-	-	-
	Thelepus sp.	-	-	+	+	-	-	-	-

Note: +, present; -, absent.

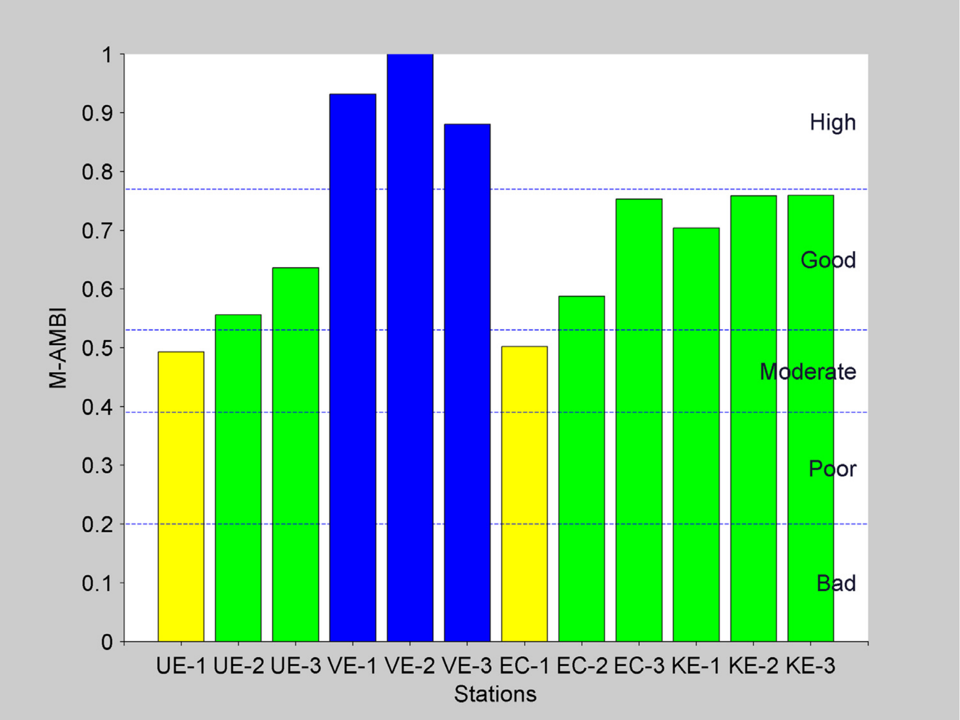

Figure 12 Multivariate-AZTI marine biotic index (M-AMBI) values indicating the ecological status for the stations of various estuaries during the study disturbance classification and M-AMBI status of the stations during the study.

and total alkalinity, HCO_3, and CO_2; and a positive linear association with CO_3. Ray et al. (2018) also reported a similar correlation with parameters combinations. Earlier studies indicated that the range of alkalinity, CO_3, and HCO_3 had increased in areas where heavy anthropogenic activities occur, corroborating the findings of the current study (Bouillon et al., 2003; Oliveira et al., 2018; Thasneem et al., 2018).

Studies conducted elsewhere reported that DIC and DOC are strongly influenced by estuarine processes (Gu et al., 2009). Accordingly, the carbon species namely DIC, DOC, and POC are essential components having an important link in biogeochemical carbon cycling between land and ocean (Wu et al., 2007). The increased concentration of CO_2 and bicarbonate ions reduces the availability of carbonate ions, which affects metabolism, growth rate, and relative abundance of polychaetes (Ho and Carpenter, 2017; Veron, 2011). In the present study, DIC concentration ranged between 835.777 (VE-3, summer) and 1734.268 μmol/kg (UE-1, monsoon) with a non-conservative decreasing trend along the salinity and pH gradient. However, as an oddity, the trend was opposite in DOC, wherein an increasing trend was found along the salinity-pH gradient, with maximum DOC during the summer and a minimum during the monsoon season. POC ranged between 32.0 (EC-1, summer) and 742.5 μmol/kg (EC-1, monsoon), generating a negative linear relationship between POC versus salinity and pH gradient. Likewise, Marescaux et al. (2018) and Ray et al. (2018) reported similar ranges of POC concentrations with a negative linear relationship for the salinity-pH gradient. With respect to pCO_2, values ranged from 89.2 (KE-3) to 1702.6 μatm (UE-1). As that of DIC, pCO_2 also exhibited a non-conservative decreasing trend along the salinity and pH gradient. With respect to pCO_2 with DIC, DOC, POC, and CO_2 concentrations, an increasing trend with a positive linear relationship was found along the pH gradient excluding DOC that showed a negative linear relationship. The study conducted by Hutchins et al. (2019) found a positive linear association versus salinity-pH gradient on large-scale drivers of DIC and POC in the Boreal river. Furthermore, low salinity was found to exacerbate negative effects of elevated CO_2 levels on growth, energy balance, and bio-mineralization of common estuarine invertebrates (Cauwet, 1991; Dickinson et al., 2012; Dutta et al., 2019; Gupta et al., 2008; Hutchins et al., 2019; Marescaux et al., 2018; Palanivel et al., 2019; Ray et al., 2018).

Total organic carbon plays a vital role in the accumulation and release of different micronutrients. It is a well-etched fact that the sediment texture determines the total organic carbon content, which in turn, influences the distribution of benthic organisms. Organic matter in sediments is an essential source of food for benthic fauna (Gray, 1974; Pearson and Rosenberg, 1978; Sanders, 1958; Snelgrove and Butman, 1994). In the present investigation, total organic carbon ranged between 3.7 (VE-2, monsoon) and 9.7 mgC/g (EC-1, summer). Sediment texture revealed clay content to be relatively high compared to sand and silt. Clay ranged between 4.25 (VE-1, monsoon) and 87.47% (KE-1, summer) followed by sand ranging from 2.37 (UE-1. monsoon) to 56.45% (VE-1, premonsoon) and silt between 5.35 and 49.34% with a peak in VE-3 (monsoon) and a trough in KE-1 (summer). Earlier authors reported that during the summer season, a large amount of organic matter settled at the bottom potentially elevating TOC levels in the study area (Khan et al., 2014; Murugesan et al., 2018; Rajasegar et al., 2002).

Multivariate analysis is considered to be an effective method to retrieve information from data sets containing more significant amounts of variance, simultaneously considering the interrelationships of several influential variables. Furthermore, these methods also allow us to analyze the patterns by relating biotic variables with abiotic patterns on spatio-temporal scales (Field, 1987). Accordingly, PCA representing the parameters DO, chlorophyll, HCO_3, alkalinity, DIC, POC, pCO_2, CO_2, sediment TOC, and clay were associated with pre-monsoon, postmonsoon, and monsoon seasons; whereas temperature, salinity, pH, BOD, CO_3, DOC, sand, and silt were associated with summer season (Supplementary Figure 1). Similar seasonal combinations of parameters were also reported by Mukherjee et al. (2014) and Sigamani et al. (2015).

The canonical correspondence analysis describes the principal tendencies in the relationship between the environmental variables and polychaete species assemblages. In component 1, parameters such as pH, salinity, DO, CO_3, sand, clay, and DOC had a positive correlation with *Cirratulus cirratus, Cossura coasta, Diopatra cuprea*, etc., as highly associated polychaetes; while other parameters such as temperature, BOD, chlorophyll, alkalinity, HCO_3, DIC, POC, pCO_2, CO_2, Sed.TOC and silt exhibited a negative correlation in component 2 with *Ancistrosyllis parva, Ancistrosyllis* sp., *Capitella capitata*, and *Cirratulus filiformis* as significantly correlated polychaete species. Similar combinations of environmental variables influencing the benthic faunal distribution were reported by Murugesan et al. (2018), Musale et al. (2015) and Sivaraj et al. (2014).

Moreover, several authors also report that the combinations of pH, salinity, and sediment variables play crucial roles in determining the distribution of the benthic community structure. Sediment-bound organic matter is related to its clay content, which in turn influences the feeding habits of the benthic fauna (Fauchald and Jumars, 1979; Flint, 1981; Gray, 1974), validating the results of the present study.

About polychaete density, the low density recorded during the monsoon season could be attributed to the inflow of copious freshwater from rivers, reducing the salinity level, and leading to unfavorable conditions. Similar trends were reported by Murugesan et al. (2018) and Sivaraj et al. (2014).

Species diversity and richness values were high during the summer and low during the monsoon season, while species evenness largely followed the trend of species diversity. Several researchers stated that terrestrial runoff during monsoon season, industrial wastes, sewage, and anthropogenic activities are known to influence the distribution of benthic organisms, reducing diversity values during the monsoon season (Musale et al., 2015; Natesan et al., 2017). With respect to polychaete diversity and $pCO_{2,}$ high fluctuation of pCO_2 in estuaries reflects similar trends of organic carbon stocks and degradation in other coastal environments as exemplified by dissolved organic carbon, oxygen saturation level, and chlorophyll-*a*. The increase in partial pressure of carbon-dioxide concentration in the aquatic environment will reduce the availability of carbonate ions, which results in minimal detrimental effects in biological and physicochemical processes (Doney et al., 2009; Frankignoulle et al., 1998). Other researchers elsewhere reported that high pCO_2/low pH reduces polychaete diversity and increases species richness values (Gambi et al., 2016; Molari et al., 2019). Accordingly, high pCO_2/low pH was recorded in stations of Uppanar and Ennore estuaries with minimum polychaete diversity. A similar range of diversity values was recorded earlier by Khan et al. (2014) in Vellar-Uppanar estuary; Sivaleela and Venkataraman (2013) in selected places long the Tamilnadu coast; Natesan et al. (2017) in Ennore coastal waters; Selvaraj et al., (2019) in Vellar and Ennore estuarine ecosystems.

Concerning salinity-zones, the members of the following polychaete families viz., Capitellidae, Eunicidae, Lumbrineridae, Nephtyidae, Nereididae, Spionidae were found to be dominant in the euhaline zone, and those of the Cirratulidae, Cossuridae, Dorvilleidae, Glyceridae, Goniadidae, Maldanidae, Onuphidae, Opheliidae, Orbiniidae, Pectinariidae, Pilargidae, Sabellidae, Syllidae, and Terebellidae families were dominant in the polyhaline zone. Accordingly, it is evident that the polychaete families with the salinity pattern stated above, indicate their ability to regulate hyper and hypo-osmotic environments in different salinity zones as described by earlier researchers (Costa et al., 1980; Freel et al., 1973; Onwuteaka, 2016; Quinn and Bashor, 1982; Richmond and Woodin, 1999; Smith, 1970 and Van Gaest et al., 2007).

AMBI-indices are a widely used tool for assessing the ecological health status of ecosystems (Borja et al., 2000). In the present study, AMBI values calculated for the benthic polychaete species fluctuated from 2.23 to 4.12. According to these values, stations UE-1, UE-2, and UE-3 in Uppanar estuary, EC-1, and EC-2 in Ennore were found to fall in the category of moderately disturbed, while other stations were in the slightly disturbed category. Similarly, M-AMBI values ranged between 0.49 and 0.99 with UE-1, UE-2, and EC-1 falling under the moderate ecological health category, while other stations fell under good and high ecological health categories. In their study, Khan et al. (2014) and Natesan et al. (2017) also reported similar ecological categories since the referred stations of Uppanar-Ennore were located near the discharge points of industrial waste, power-plant discharge of coolant water, indiscriminate discharge of untreated municipal waste, terrestrial river runoff and anthropogenic activities which could have generated variations in the benthic community structure resulting in the dominance of pollution tolerant benthic polychaete groups in the disturbed category.

5. Conclusion

The present study provides benchmark data on the distribution of polychaetes in relation to pH-salinity gradients in the studied estuaries of Tamilnadu. The role of the pH-salinity gradient in conjunction with sediment characteristics on polychaete distribution is intriguing, as there was a decrease in polychaete diversity during monsoonal months, but a few opportunistic polychaete species were found to occur in extremely large numbers in the Uppanar and Ennore estuaries. Although some light has been shed on the role of the salinity-pH gradient on the polychaete community in selected estuaries, more research into the interaction modes of biotic/abiotic processes is needed to determine the accuracy of polychaete occurrence along salinity gradients/zones of biological, chemical, and physical processes.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at https://doi.org/10.1016/j.oceano.2022.01.001.

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