



Evaluation of water pollution in the estuary and adjacent coastal Bay of Bengal using water quality index and its implication to sustainable ecosystem management

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Abstract

Estuaries and coastal environment in the Bay of Bengal are affected by wide range of contaminants due to increased anthropogenic activity from a budding population in the coastal region. Sixteen physico-chemical and biological parameters were measured from 14 stations during four seasons like summer, monsoon, post-monsoon and winter along Mahanadi River, creek, estuarine and adjacent coastal ecosystem in 2011 and 2012. The results indicate that average lower value of pH (6.61 ± 0.68) was in winter, and dissolved oxygen (DO; $3.89 \pm 2.01 \text{ mg L}^{-1}$) was during monsoon in the ecosystem compared to the other season, whereas average higher concentration of Biochemical Oxygen Demand (BOD; $5.92 \pm 2.62 \text{ mg L}^{-1}$), nitrate ($68.77 \pm 30.35 \text{ } \mu\text{M}$), ammonium ($43.50 \pm 21.46 \text{ } \mu\text{M}$) and Phosphate ($39.73 \pm 10.63 \text{ } \mu\text{M}$) were found in the creek during post-monsoon. The ratio between nitrate and phosphate (N:P) declined in entire ecosystem of the study region indicated nutrient limiting due to the inorganic load into the system. The nutrients and phytoplankton biomass (Chlorophyll-*a*) show a strong positive correlation ($r=0.591$) and negative correlation ($r=-0.549$) with BOD, respectively. Nutrients behaved non-conservatively and played a significant role in the depletion of DO. Factor analysis shows that loading activities of water quality parameters are mainly related to the major organic pollution, inorganic pollution and nutrients load into the ecosystem, whereas the cluster analysis and water quality index (WQI) resulted that the study region ecosystem has triggered alarm, due to various significant levels of contaminants. Hence, proper industrial management along with necessary measures is recommended for estuary and coastal environment ecosystem from socioeconomic disaster and sustainable ecosystem management.

Keywords Factor analysis · Industry · Nutrients · Pollution: water quality index · Tropical estuary · Water quality

Introduction

The extreme range of environmental problems is now a matter of serious international concern. These include atmospheric pollution, marine pollution, global warming and depletion of ozone, which are threatening to the ecosystem. The high growth rate of population, urbanization and industrials in the river estuary and coastal regions have experienced serious anthropogenic pollution (Jenssen 2003).

Water is an essential element of human and industrial development and is an integral part of the environment (Das and Acharya 2003).

The environmental factors, such as topography, water flow and stratification, salt, oxygen, temperature and water-soluble nutrients, regulate the formation of the regional biota (Karande 1991). The rate of recurrence in river, estuary and adjacent coastal waters, shows a significant seasonal variations depending on the regional rainfall conditions, volume uptake, tidal influences, various abiotic and biotic processes. The amount of fresh water infiltration affects the structural cycle of different coastal areas (Schofield et al. 2018). The physico-chemical properties of water are interrelated biological activities created by the active or passive movements of living aquatic and semi-aquatic organisms and their moving in various ways in different spatial and temporal scales (Gounand et al. 2017; Schofield et al. 2018). Over the past few decades, there has been a dramatic increase in

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demand for fresh water due to rapidly increasing of population and industrial growth (Ramakrishnaiah et al. 2009). People's health is threatened by many agricultural development activities, especially in terms of over-fertilization and adverse conditions (Okeke and Igboanua 2003). Rivers, estuary and coastal waters play an important role in transporting large amounts of fresh water, thus filling the water table regularly. Estuary is the complex ecosystem because of the high dynamic environment. It is managing the physical and chemical properties due to nutrients input from river and sea water (Jiang 2011). Estuaries, which form transitional zones where fresh water from land drainage mixes with seawater and create the ecologically productive areas, are among the most significant coastal ecosystems (Kennish 2002). Numerous anthropogenic disturbances have an impact on estuarine habitats, altering habitat and changing the structure and dynamics of biotic communities. Over population and unregulated development in coastal watersheds, as well as human activities in estuary embayment, usually cause environmental concerns in these systems (Kennish 2002; McQuatters-Gollop et al. 2009; Bužančić et al. 2016). It is a most important to take sustainable steps for features changes in certain area with tide flow and current resulting from seasonal and inter-annual dynamics into the ecosystem (Bužančić et al. 2016). Anthropogenic activities affect nearly all estuaries in some way, and they will likely become more widespread and intense over the next 25 years, as the coastal population is predicted to reach six billion people by 2025 (Kennish 2002).

The Mahanadi River system is the third largest in the Indian peninsula and the largest river in the Odisha region. The basin ($80^{\circ} 30' - 86^{\circ} 50' E$ and $19^{\circ} 20' - 23^{\circ} 35' N$) stretches in an area of about $141,600 \text{ km}^2$, length of 851 km and an annual runoff $50 \times 10^9 \text{ m}^3$ with a peak discharge of $44,740 \text{ m}^3 \text{ s}^{-1}$ (Sundaray et al. 2009), which is approximately 4.3% of the total land area. The annual average rainfall is 150 cm with 85% during the south-west monsoon (Swain 2014). Mahanadi estuary flows a distance of 494 km and is the largest river system in Odisha, The estuary is narrow (1.13 km at the sea end) and the tide is semidiurnal in nature along with vertical tide varies from 1.45 to 2.2 m (at mouth region). The annual Mahanadi river flow is $66,640 \times 10^6 \text{ m}^3$ water and accounted about 75% of water during monsoon (Singh and Sinha 1996) and is a large sedimentary site near the Bay of Bengal (BOB). There are about 34 cities, towns and urban settlements are situated around the Mahanadi surroundings in the basement of Odisha. The estuary serves as a major source of domestic water supply for the towns of Cuttack, Sambalpur and Paradip with a population of about 0.85 million (Sundaray et al. 2006). Three major urban areas (Cuttack, Sambalpur and Paradip), the Paradip port, fish landing harbor, and many industrials that situated on the

river bank near estuary are contributing the release of untreated sewage and effluents to the coastal water (Panda et al. 2005; Sundaray et al. 2009). Atharabanki Creek is very important in the study of water pollution because the waste from Paradip Phosphate Ltd (PPL), Indian Farmers and Fertilizer Cooperative (IFFCO) Ltd, SKOLB receives, sewage from PPL Township and Paraded Port Trust (PPT) is being discharged into the river joining Mahanadi estuary and meeting in the Bay of Bengal (Sundaray et al. 2009). In the estuarine environments of Mahanadi and its adjacent coastal water, the chemical oceanographic studies were made in addition to biological and chemical investigations in some specific points along the estuary (Nanda et al. 2001; Nayak et al. 2004; Sundaray et al. 2009; Pradhna et al. 2009). There is no detailed study on the evolution of water quality in the water of Atharabanki Creek, Mahanadi upstream, estuary and its adjacent coastal until.

There have been obvious gaps in these investigations of the designated research region, which includes Atharabanki Creek, the Mahanadi upstream, and the estuary stretch from upstream to mouth. This seasonality has been adapted by the estuarine ecology and its accompanying natural habitat (Naik et al. 2020). Water quality is considered as a vital role in determining the health and state of the marine environment. Hence, the present study explores on a detailed hydrographical features and significant point sources of water pollution in the Mahanadi River, creek, estuary and adjacent coastal water. This study will help in understanding and assessing the pollution load due to the different urban and industrial development and also facilitate for better management to create a healthy environment and pollution free ecosystem in the region.

Materials and methods

Study area

The Mahanadi River is one among the major estuaries along east coast of India which meet the Bay of Bengal at Paradip (Fig. 1). The estuary is narrow (1.13 km at the sea end), and the tide is semidiurnal in a nature. The range of vertical tide at the mouth varies from 1.45 to 2.2 m. The tidal estuarine part section of the river covers an area of 40 km and has a basin area of 9 km^2 . The study region has four distinct seasons such as summer (March–May), monsoon (June–September), post-monsoon (October–December) and winter (January and February) (https://en.m.wikipedia.org/wiki/Climate_of_India#). Monthly rainfall and fresh water discharge data during the investigation (2011 and 2012) were collected from the Department of Water resources, Bhubaneswar, India (Fig. 2).



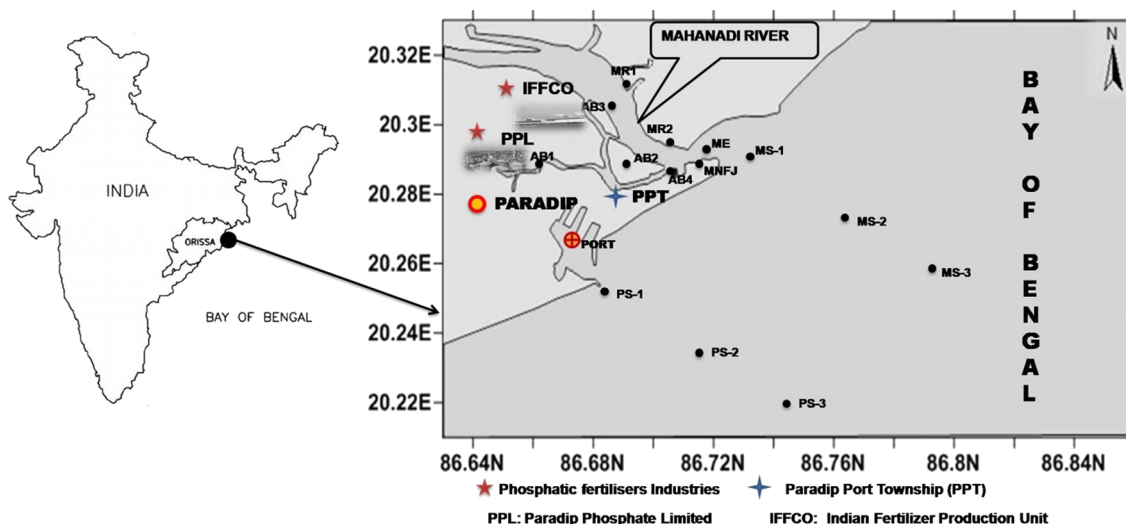
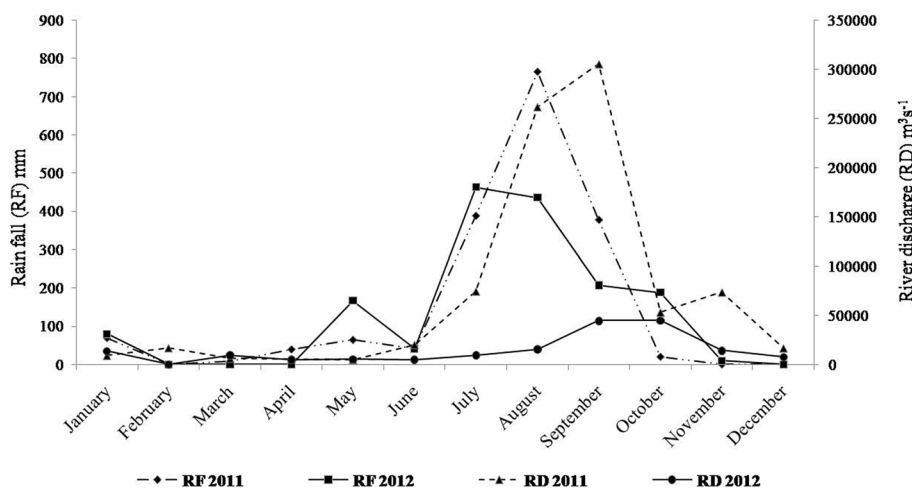


Fig. 1 Location map of study site along the Mahanadi River, estuary and coastal ecosystem

Fig. 2 Monthly variation of the rain fall and river discharge at the study site during 2011 and 2012 (RF- rainfall, RD- river discharges)



Sampling technique

The surface water samples were collected seasonally (summer, monsoon, post-monsoon and winter) from fourteen selected stations located in the Mahanadi upstream (2 stations), creek (4 stations), estuary (2 stations) and adjacent coastal region (6 stations) using mechanized boat during 2011 and 2012. The sampling locations are divided into four separate regions based on salinity distribution such as Atharabanki creek (AB1–AB4), Mahanadi upstream (MR1 to MR2), Mahanadi estuary (MNFJ and ME) and its adjoining coastal (MS1 to MS3 and PS1 to PS3) from the estuary to 1 km, 3 km and 5 km, respectively (Fig. 1), and Global position station (GPS) is represented in Table 1.

Analysis technique

Surface water samples were collected using pretreated polypropylene bottles and stored at 4 °C for further laboratory analysis. In situ measurements of the temperature (air and water), pH, dissolved oxygen (DO) and salinity are carried out using multi probe water quality kit (WTW Multi Lab P4). Biological oxygen demand (BOD), Total suspended solids (TSS), nutrients, and chlorophyll-*a* are analyzed by following the standard protocols (APHA 1998; Grasshoff et al. 1999). Nutrients are analyzed by colorimetric method using spectrophotometer (PerkinElmer LAMBDA 365UV) and standardized with reference material (MOOS-3). All analyzed procedure and precision are presented in

Table 1 Geographical position system (GPS) locations in the study area

Stations	Stations	Longitude	Latitude	Locations
AB1	St. 1	20° 17' 31.54"	86° 38' 45.32"	Creek
AB2	St. 2	20° 17' 30.25"	86° 40' 45.13"	Creek
AB3	St. 3	20° 18' 00.06"	86° 40' 56.44"	Creek
AB4	St. 4	20° 17' 17.47"	86° 42' 05.19"	Creek
MR1	St. 5	20° 18' 20.86"	86° 41' 15.59"	River
MR2	St. 6	20° 17' 44.71"	86° 41' 42.08"	River
MNFJ	St. 7	20° 17' 22.77"	86° 42' 24.13"	Fishing jetty
ME	St. 8	20° 17' 36.42"	86° 42' 29.65"	Estuary
MS-1	St. 9	20° 17' 29.01"	86° 43' 07.03"	Shore
MS-2	St. 10	20° 15' 33.68"	86° 45' 08.90"	Near shore
MS-3	St. 11	20° 13' 45.94"	86° 47' 18.78"	Near shore
PS-1	St. 12	20° 15' 15.66"	86° 40' 06.74"	Shore
PS-2	St. 13	20° 12' 57.78"	86° 41' 23.66"	Near shore
PS-3	St. 14	20° 10' 59.34"	86° 43' 20.38"	Near shore

AB: Atharabanki creek, MR: Mahanadi upstream, ME: Mahanadi estuary,

MC: Mahanadi coastal, PDC: Paradip coastal and MNFJ: Mahanadi fishing jetty

Table 2. Sample analysis was carried out in triplicate, and the mean value with standard deviation was considered for interpretation.

Multivariate statistical analysis

The assessment of the water quality of the region and identification of the pollution source was carried out by using multivariate statistical analysis. Hierarchical agglomerative Cluster Analysis (CA) was performed on the normalized data set by means of the employing Ward's method, using squared Euclidean distances as a measure of similarity. The spatial variability of water quality in the river, estuary, creek and coast is determined from Factor analysis, cluster analyses and correlation

analysis performed using the software IBM SPSS 20. Regression analysis was performed to understand the conservative and non-conservative behavior of the water quality parameters.

Water quality index (WQI)

The water quality index is a useful tool for monitoring water quality that is frequently used in water management. The Canadian Council of Ministers of the Environment water quality index (CCME-WQI) is one of the most widely used indices in the world. The CCME-WQI is made up of three variables F1, F2, and F3. The "Scope (F1)" indicates the amount of noncompliance with water quality guidelines across the time period of interest. The percentage of individual tests that do not match the objectives is represented by the "Frequency (F2)." The "Amplitude (F3)" shows the amount by which failed tests do not meet their objectives.

$$F1 = \left(\frac{\text{Numbers of failed variables}}{\text{total numbers of variables}} \right) \times 100 \quad (1)$$

$$F2 = \left(\frac{\text{Numbers of failed tests}}{\text{total numbers of tests}} \right) \times 100 \quad (2)$$

Calculation of Excursion: Excursion is the number of times by which an individual concentration is greater than (or less than, when the objective is a minimum) the objective.

$$\text{excursion} = \left(\frac{\text{failed test value}}{\text{objectives}} \right) - 1 \quad (3)$$

Calculation of Normalized Sum of Excursions- (nse): It is the collective amount by which individual tests are out of compliance (Wang et al. 2016). It is calculated by summing the excursions of individual tests from their objectives and dividing by the total number of tests (both those meeting objectives and those not meeting objectives)

Table 2 Analyzed procedure and precision Water and biological quality parameters

Sl. no	Parameter	Analyzed procedure	Precision
1	Temperature	Portable multi-parameter probe	± 0.01 °C
2	Salinity	Mohr-Knudsen titration	± 0.004 ‰
3	Dissolved Oxygen (DO)	Winkler's titration	± 0.1 mg/l
4	pH	Portable multi-parameter probe	± 0.005
5	Nitrite (NO ₂)	Azo dye method (MOOS-3)	± 0.006 µM
6	Nitrate (NO ₃)	Reduction to NO ₂ -followed by Azo dye method (MOOS-3)	± 0.06 µM
7	Ammonium (NH ₄ ⁺)	Indo-phenol blue method (MOOS-3)	± 0.06 µM
8	Phosphate (PO ₄)	Phospho-molybdenum blue method (MOOS-3)	± 0.003 µM
9	Silicate (SiO ₄)	Silico-molybdenum blue method (MOOS-3)	± 0.01 µM
10	Chlorophyll <i>a</i> (Chl- <i>a</i>)	Spectrophotometry	± .05 mg/m ³

$$nse = \frac{\sum_{i=1}^n \text{excursion}}{\text{Number of tests}} \quad (4)$$

$$F3 = \left(\frac{nse}{0.01nse + 0.01} \right) \quad (5)$$

Equation (6) depicts the mathematical formulation of the CCME-WQI:

$$\text{CCME} - \text{WQI} = 100 - \frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \quad (6)$$

where F1 is the percentage of parameters whose guidelines are not met at least once, as a percentage of the total number of parameters measured;

F2 is the percentage of individual tests that do not meet their respective guideline ("failed tests");

F3 is the amount by which the failed test values do not meet their respective guideline.

Sl. no.	Grade	CCME WQI value	Impacts
1	Excellent	95–100	Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels
2	Good	80–94	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels
3	Marginal	45–64	Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels
4	Poor	0–44	Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels

To scale the index from 0 to 100, a scaling factor of 1.732 is used. A recent work (CCME 2001) fully defined the detailed calculation process for F1, F2, and F3. The CCME WQI value of water quality is classified into one of the following categories:

Results and discussion

Physico-chemical characteristics

The results of physico-chemical parameters, i.e., temperature (Air and water), Total suspended solids (TSS), pH,

salinity, Dissolved oxygen (DO) and Biochemical oxygen demands (BOD), are presented in Fig. 3. During the present study, the air temperature varied from 24.80 ± 3.15 °C during winter to 32.84 ± 1.40 °C during summer. Compared to different regions, the water temperature remained slightly higher for coastal region with 25.91 ± 2.82 °C during winter to 32.84 ± 1.40 °C during summer. Lowest water temperature (23.65 ± 3.87 °C) was recorded from the upstream during winter season, and increased to the highest (30.52 ± 0.80 °C) during summer in the coastal water. The pH ranged between 6.61 ± 0.68 to 7.13 ± 0.64 in creek, 7.23 ± 0.26 to 7.73 ± 0.31 in upstream, 7.73 ± 0.17 to 8.05 ± 0.07 in estuary and 8.04 ± 0.07 to 8.12 ± 0.10 in coastal region, respectively (Table 3). The highest pH of 8.12 was recorded from coastal region during post-monsoon and winter whereas lowest 6.61 was recorded from the creek during winter. The salinity fluctuation was highest (7.58 ± 2.70) in estuary during monsoon to summer (22.88 ± 2.77). Similarly, salinity of upstream/river ranged between 3.63 ± 0.43 during monsoon to 18.39 ± 1.88 during summer. In the creek and coastal region, salinity ranged between 3.86 ± 2.51 and 18.36 ± 6.58 , respectively, during monsoon to 16.32 ± 4.54 and 28.30 ± 2.70 , respectively, during winter. DO concentration was recorded low for the creek with the lowest 3.89 ± 2.01 mg L⁻¹, during monsoon to 5.56 ± 0.49 mg L⁻¹, during summer. The highest DO concentration was remained high in the coastal waters ranging between 7.10 ± 0.38 mg L⁻¹ during post-monsoon to 7.56 ± 0.51 mg L⁻¹ during summer. BOD was found highest in the creek ranging from 5.27 ± 2.87 mg L⁻¹ in winter to 5.92 ± 2.62 mg L⁻¹ in monsoon. Lowest BOD was recorded from the coastal region with a highest of 1.20 ± 0.79 mg L⁻¹, in winter to 2.29 ± 0.76 mg L⁻¹ in monsoon.

In 2011, the highest concentration of total suspended solids (TSS) found 55.75 ± 8.06 mg L⁻¹, 51 ± 0.01 mg L⁻¹, $45.9,4 \pm 5.76$ mg L⁻¹, and 37.57 ± 6.33 mg L⁻¹, in monsoon (Fig. 4) and lowest 15.75 ± 3.40 mg L⁻¹, 11.50 ± 0.71 mg L⁻¹, 16.25 ± 3.07 mg L⁻¹, and 14.56 ± 5.59 mg L⁻¹, in summer (Fig. 4) for the creek, upstream, estuary and costal region, respectively. Similarly, in 2012 the higher value of TSS found 82.25 ± 15.95 mg L⁻¹, 49.5 ± 0.71 mg L⁻¹, 69.17 ± 11.26 mg L⁻¹ and 29.06 ± 12.37 mg L⁻¹, in monsoon and lower value are recorded 38 ± 5.76 mg L⁻¹, 9.50 ± 0.71 mg L⁻¹, and 16.30 ± 2.75 mg L⁻¹ in summer except estuarine water (9.30 ± 3.42 mg L⁻¹) in winter.

Nutrients

In 2011, the highest nitrite concentration was recorded from the creek ranging from 2.50 ± 1.73 μM in summer to 9.70 ± 1.71 μM during monsoon (Fig. 4, Table 4). Similarly,



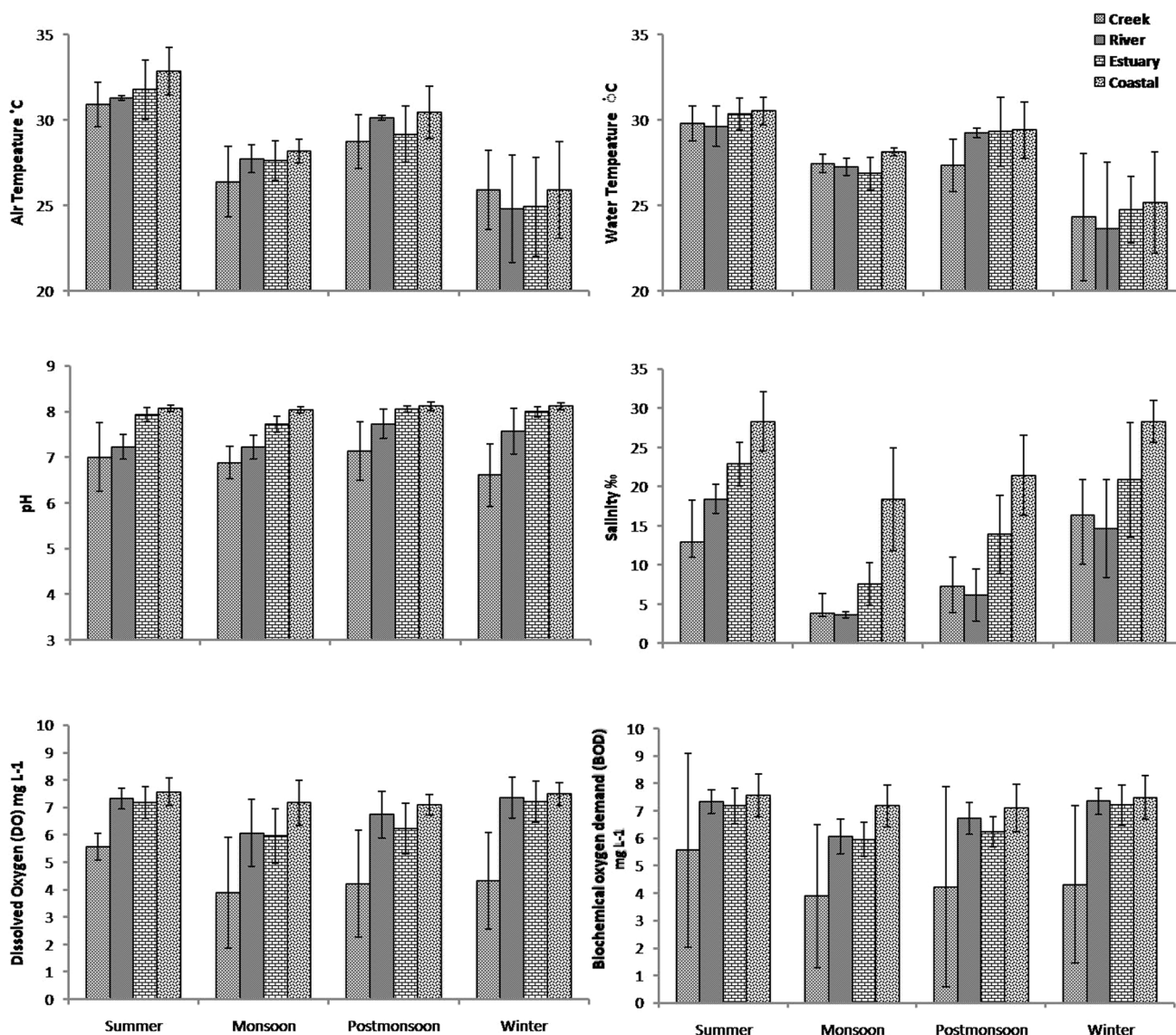


Fig. 3 Seasonal and temporal variation of the physico-chemical parameters in estuary, Mahanadi River and coastal water during the study period

in the upstream, estuary and coastal region, the nitrite concentration was low of $0.67 \pm 0.03 \mu\text{M}$, $0.31 \pm 0.22 \mu\text{M}$ and $0.16 \pm 0.24 \mu\text{M}$, respectively, during summer and was higher as $4 \pm 0.04 \mu\text{M}$, $2.83 \pm 1.77 \mu\text{M}$ and $1.71 \pm 0.78 \mu\text{M}$, respectively, during monsoon. In 2012, the highest nitrite concentration was recorded from creek ranging from $1.79 \pm 0.53 \mu\text{M}$ in summer to $10.89 \pm 3.65 \mu\text{M}$ during winter (Fig. 4, Table 5). Similarly, in the upstream, estuary and coastal region, the nitrite concentration was low as $0.89 \pm 0.05 \mu\text{M}$, $0.51 \pm 0.26 \mu\text{M}$ and $0.18 \pm 0.08 \mu\text{M}$, respectively, during summer and was high as $3.94 \pm 0.56 \mu\text{M}$, $4.70 \pm 3.59 \mu\text{M}$ and $1.27 \pm 0.42 \mu\text{M}$, respectively, during monsoon.

In 2011, the highest nitrate concentration was recorded from the creek ranging from $15.25 \pm 4.57 \mu\text{M}$ in summer to $65.50 \pm 36.45 \mu\text{M}$ during monsoon (Fig. 4). In the same time, in

the upstream and estuary, the nitrate concentration was low as $2 \pm 0.05 \mu\text{M}$ and $3.08 \pm 2.06 \mu\text{M}$, respectively, during summer and was higher as $11 \pm 1.41 \mu\text{M}$ and $11.59 \pm 5.93 \mu\text{M}$, respectively, during monsoon, whereas, in the coastal region, the lowest concentration ($2.28 \pm 1.22 \mu\text{M}$) was recorded during summer and highest ($4.19 \pm 2.61 \mu\text{M}$) was recorded during winter (Fig. 4). In 2012, the higher nitrate concentration was recorded from creek ranging from $24.13 \pm 14.1 \mu\text{M}$ to $68.77 \pm 30.35 \mu\text{M}$ from summer to post-monsoon (Fig. 4). In the upstream, estuary and coastal region, the nitrate concentration was lower of $1.05 \pm 0.39 \mu\text{M}$, $3.61 \pm 2.21 \mu\text{M}$ and $2.39 \pm 0.60 \mu\text{M}$, respectively, during winter and was higher as $21.05 \pm 3.22 \mu\text{M}$, $18.31 \pm 10.93 \mu\text{M}$ and $10.14 \pm 5.71 \mu\text{M}$, respectively, during monsoon.



Table 3 Seasonal and spatial variation Physico-chemical parameters along the study region

		Summer	Monsoon	Post-monsoon	Winter
AT °C	Creek	30.93 ± 1.30	26.39 ± 2.07	28.73 ± 1.58	25.90 ± 2.32
	River	31.28 ± 0.15	27.73 ± 0.82	30.10 ± 0.14	24.80 ± 3.15
	Estuary	31.78 ± 1.75	27.63 ± 1.16	29.16 ± 1.64	24.91 ± 2.91
	Coastal	32.84 ± 1.40	28.18 ± 0.69	30.44 ± 1.54	25.91 ± 2.82
WT °C	Creek	29.79 ± 1.03	27.45 ± 0.52	27.34 ± 1.51	24.33 ± 3.73
	River	29.63 ± 1.19	27.25 ± 0.50	29.23 ± 0.29	23.65 ± 3.87
	Estuary	30.36 ± 0.93	26.86 ± 0.94	29.31 ± 2.02	24.75 ± 1.96
	Coastal	30.52 ± 0.80	28.14 ± 0.24	29.41 ± 1.65	25.17 ± 2.97
pH	Creek	7.00 ± 0.76	6.88 ± 0.35	7.13 ± 0.64	6.61 ± 0.68
	River	7.23 ± 0.26	7.23 ± 0.26	7.73 ± 0.31	7.57 ± 0.50
	Estuary	7.93 ± 0.15	7.73 ± 0.17	8.05 ± 0.07	8.00 ± 0.11
	Coastal	8.06 ± 0.07	8.04 ± 0.07	8.12 ± 0.10	8.12 ± 0.08
Sal ‰	Creek	12.90 ± 5.33	3.86 ± 2.51	7.26 ± 3.75	16.32 ± 4.54
	River	18.39 ± 1.88	3.63 ± 0.43	6.13 ± 3.35	14.63 ± 6.22
	Estuary	22.88 ± 2.77	7.58 ± 2.70	13.90 ± 5.02	20.87 ± 7.34
	Coastal	28.27 ± 3.79	18.36 ± 6.58	21.45 ± 5.09	28.30 ± 2.70
DO mg L ⁻¹	Creek	5.56 ± 0.49	3.89 ± 2.01	4.22 ± 1.94	4.32 ± 1.76
	River	7.33 ± 0.38	6.07 ± 1.23	6.74 ± 0.86	7.36 ± 0.75
	Estuary	7.18 ± 0.58	5.96 ± 1.01	6.23 ± 0.91	7.21 ± 0.76
	Coastal	7.56 ± 0.51	7.18 ± 0.82	7.10 ± 0.38	7.49 ± 0.43
BOD mg L ⁻¹	Creek	5.41 ± 3.54	5.92 ± 2.62	5.91 ± 3.64	5.27 ± 2.87
	River	2.32 ± 0.42	3.41 ± 0.63	2.50 ± 0.58	1.27 ± 0.47
	Estuary	2.08 ± 0.65	3.34 ± 0.61	2.56 ± 0.54	1.79 ± 0.73
	Coastal	1.66 ± 0.79	2.29 ± 0.76	1.47 ± 0.87	1.20 ± 0.79
TSS mg L ⁻¹	Creek	26.88 ± 12.67	69.00 ± 18.37	44.63 ± 10.89	27.00 ± 11.35
	River	10.50 ± 1.29	50.25 ± 0.96	33.75 ± 13.79	12.75 ± 3.77
	Estuary	16.07 ± 5.00	57.55 ± 14.92	31.22 ± 10.96	16.60 ± 9.61
	Coastal	16.06 ± 5.66	33.29 ± 10.36	23.51 ± 12.40	13.04 ± 6.74

The concentration of ammonia ranged between $1 \pm 0.02 \mu\text{M}$ and $43.50 \pm 21.46 \mu\text{M}$ in the upstream of the creek during 2011. The concentration of ammonia persisted higher in the creek region during all the seasons. The higher concentration of ammonia was recorded for all the stations during monsoon which are $43.50 \pm 21.46 \mu\text{M}$, $10 \pm 0.01 \mu\text{M}$, $17.37 \pm 7.31 \mu\text{M}$ and $11.39 \pm 7.50 \mu\text{M}$, respectively (Fig. 4), for the creek, upstream, estuary and coastal region. The concentration of ammonia was lower during summer season and continued the trend in 2012. The higher concentration of ammonia was recorded during monsoon; however, lower concentration was recorded during winter. The concentration of ammonia persisted higher in the creek region as $15.12 \pm 6.50 \mu\text{M}$, $38.55 \pm 27.62 \mu\text{M}$, $42.63 \pm 26.42 \mu\text{M}$ and $36.51 \pm 26.24 \mu\text{M}$ (Fig. 4) during summer, monsoon, post-monsoon and winter, respectively.

The concentration of total nitrogen (TN) was remained high in the creek region during the study period. In 2011, the concentration of TN ranged between $67.98 \pm 23.90 \mu\text{M}$ during winter to $156.50 \pm 71.22 \mu\text{M}$ during monsoon in the creek region. In the upstream at estuary and coastal

the TN ranged from $21 \pm 0.04 \mu\text{M}$, $31.24 \pm 8.82 \mu\text{M}$ and $29.28 \pm 13.54 \mu\text{M}$, respectively, during summer (Fig. 5a) to post-monsoon ($62.82 \pm 19.03 \mu\text{M}$) and monsoon ($42.46 \pm 23.24 \mu\text{M}$) (Fig. 4). The concentration remained higher in the creek during 2012 with a magnitude of ($170.12 \pm 95.33 \mu\text{M}$) during winter and low concentration ($80.48 \pm 16.8 \mu\text{M}$) during summer. Similarly, in the estuary, the higher concentration ($78.88 \pm 15.33 \mu\text{M}$) during winter and lower concentration ($40.14 \pm 3.67 \mu\text{M}$) during summer. In the upstream at coastal region, TN ranged between $33.19 \pm 4.15 \mu\text{M}$ and $22.84 \pm 5.32 \mu\text{M}$ during summer to $50.13 \pm 7.04 \mu\text{M}$ and $57.80 \pm 21.29 \mu\text{M}$ during post-monsoon (Fig. 4).

The phosphate ($\text{PO}_4\text{-P}$) and total phosphate (TP) concentrations were maximum in both the years at creek during all seasons (Fig. 4). In 2011, the concentration of $\text{PO}_4\text{-P}$ ranged from $29.63 \pm 10.85 \mu\text{M}$ (summer) to $39.73 \pm 10.63 \mu\text{M}$ (post-monsoon) in the creek, $11.28 \pm 0.08 \mu\text{M}$ (winter) to $13.50 \pm 2.12 \mu\text{M}$ (monsoon) in the upstream, $15.77 \pm 4.06 \mu\text{M}$ (summer) to $24.06 \pm 7.23 \mu\text{M}$ (post-monsoon) the estuary and



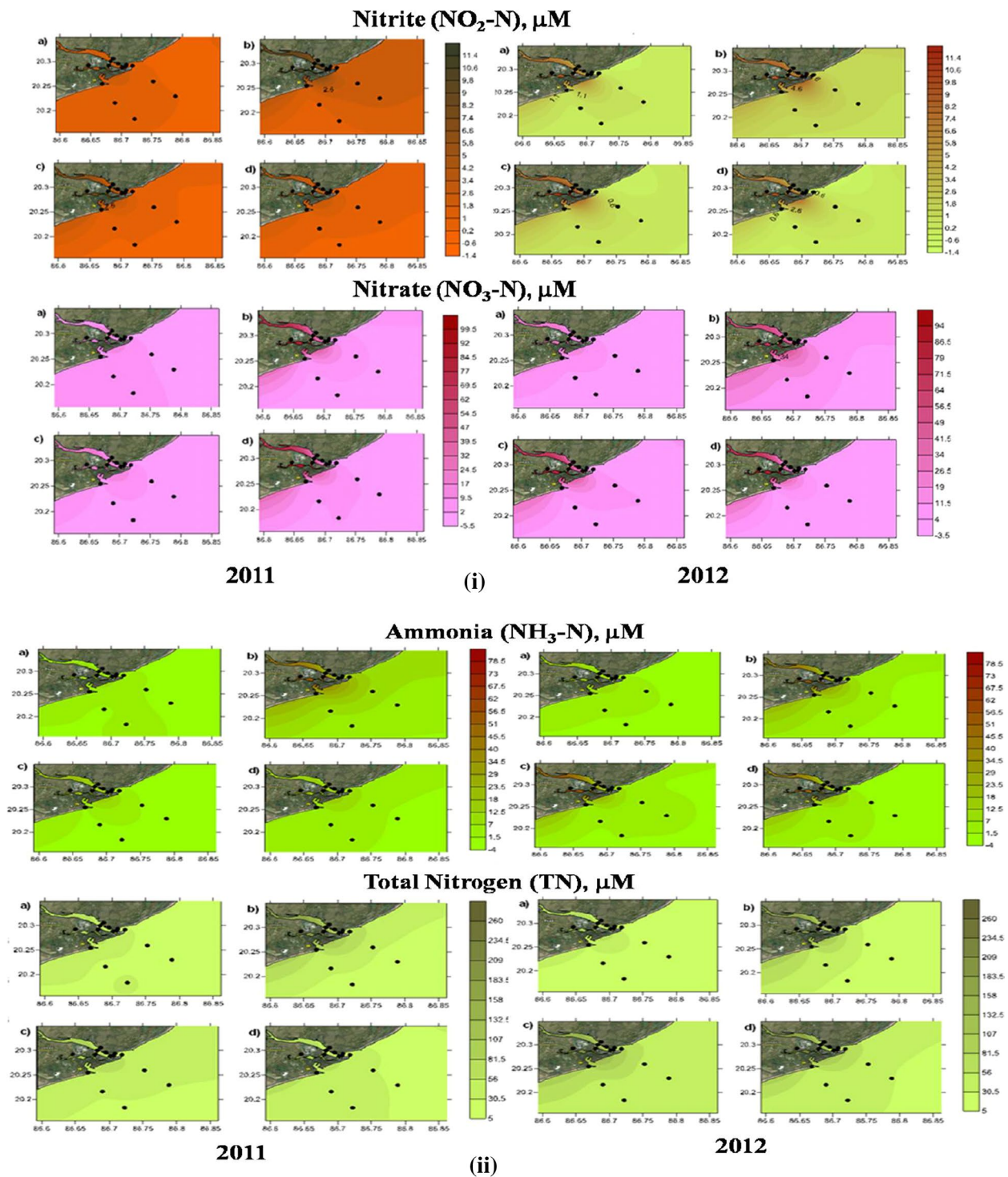


Fig. 4 (i) Seasonal and spatial distribution Nitrite and nitrate in estuary, Mahanadi River and coastal water ecosystem during the study period **a** summer **b** monsoon **c** post-monsoon and **d** winter. (ii) Seasonal and spatial distribution of ammonia and total nitrogen in estuary, Mahanadi River and coastal water ecosystem during the study period **a** summer **b** monsoon **c** Post-monsoon and **d** winter. (iii) Seasonal and spatial distribution of phosphate and total phosphate in estuary, Mahanadi River and coastal water ecosystem dur-

ing the study period **a** summer, **b** monsoon, **c** post-monsoon and **d** winter. (iv) Seasonal and spatial distribution of silicate and fluoride in estuary, Mahanadi River and coastal water ecosystem during the study period **a** summer, **b** monsoon, **c** post-monsoon, and **d** Winter. (v) Seasonal and spatial distribution of Total suspended solids and chlorophyll-*a* in estuary, Mahanadi River and coastal water ecosystem during the study period **a** summer, **b** monsoon, **c** post-monsoon and **d** Winter



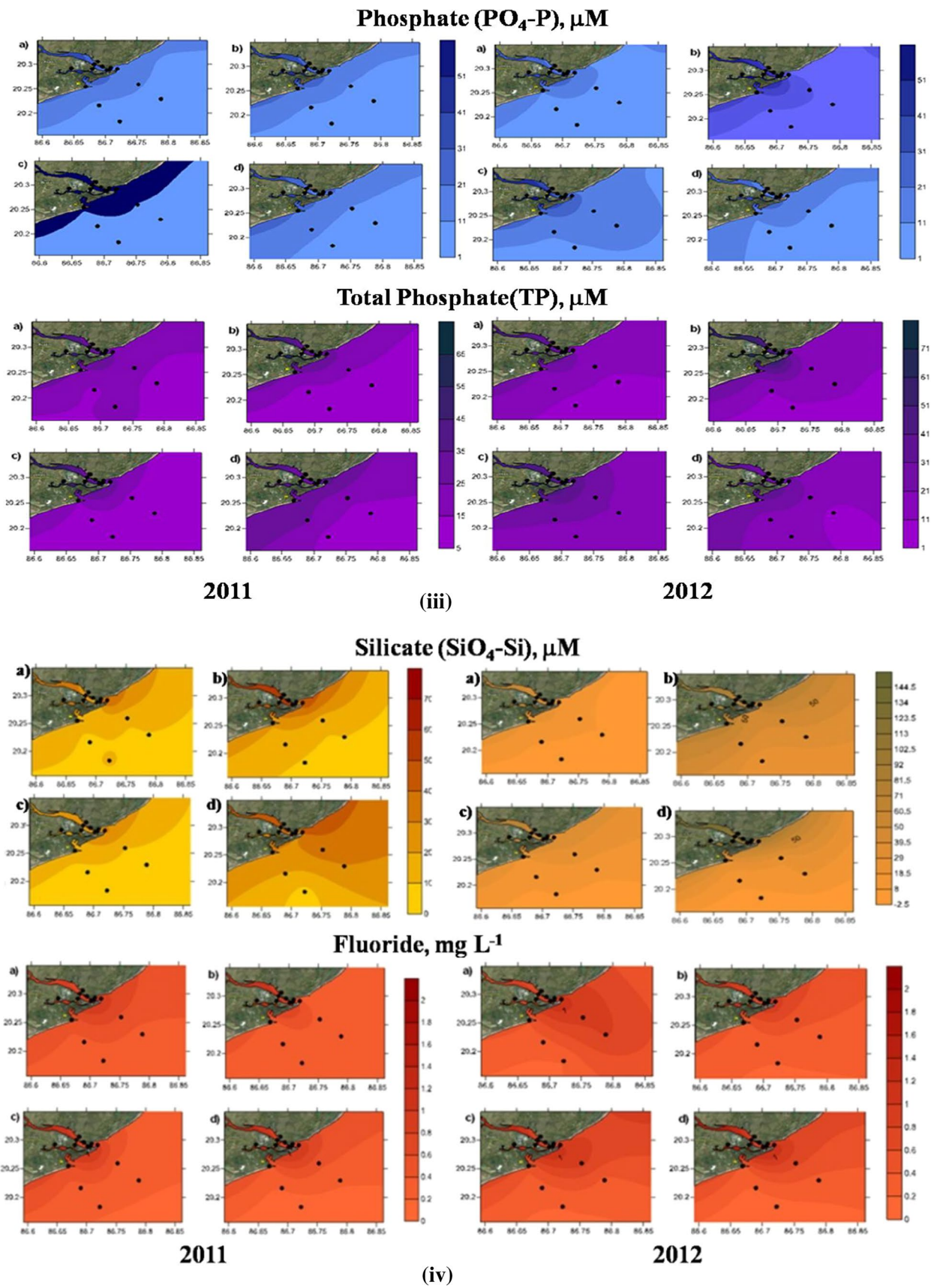


Fig. 4 (continued)

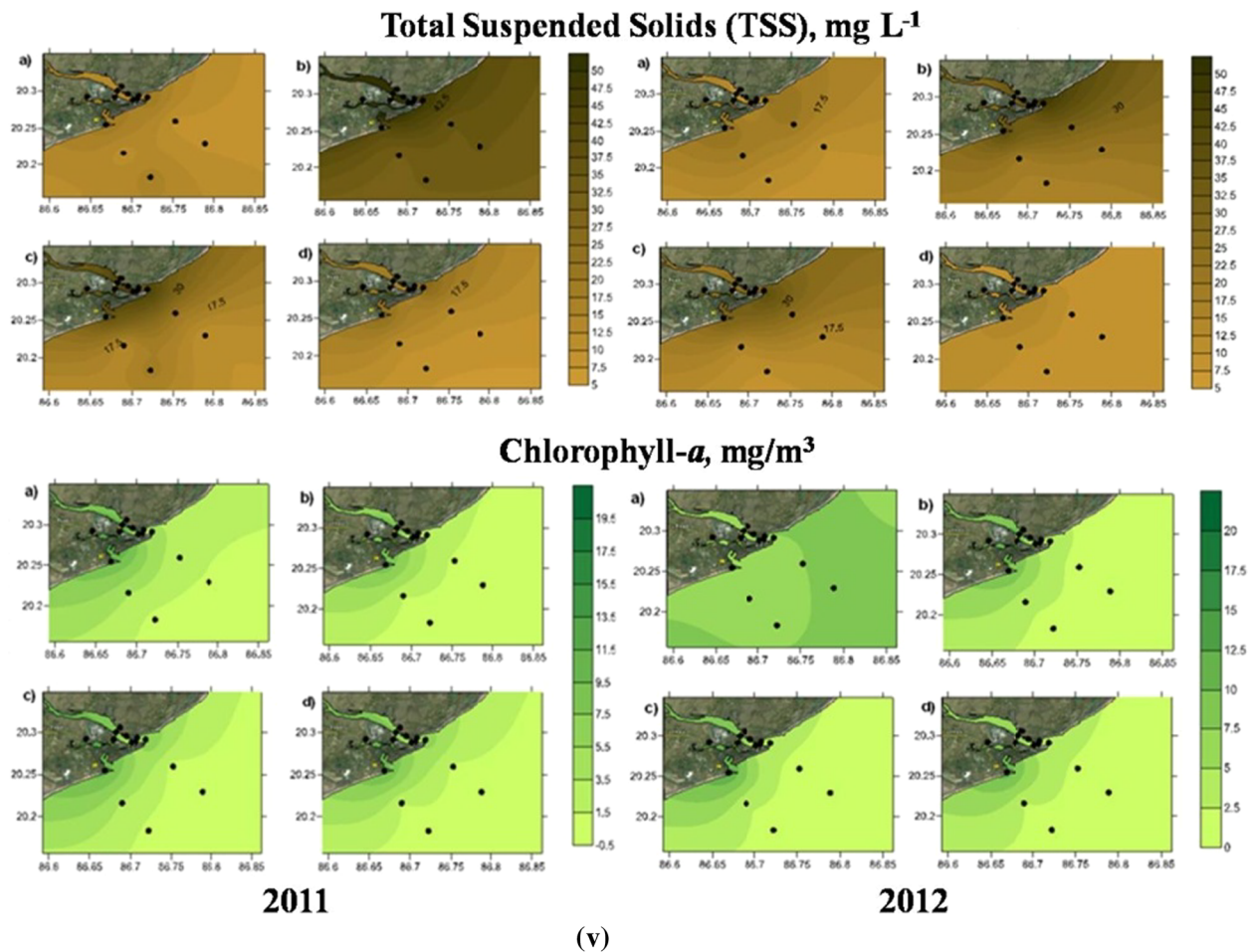


Fig. 4 (continued)

10.93 ± 5.16 μM (summer) to 12.84 ± 7.70 μM (winter) in the coastal water, respectively (Table 4). In 2012, creek and estuary ranged from 26.61 ± 11.51 μM and 16.31 ± 4.80 μM during winter to 48.12 ± 13.49 μM and 28.34 ± 4.88 μM in post-monsoon. In upstream, the lower concentration (6.54 ± 1.95 μM) was recorded during summer and higher concentration (13.21 ± 2.83 μM) during monsoon. Similarly, lower concentration (8.72 ± 5.94 μM) during summer and higher concentration (16.02 ± 5.96 μM) were found during monsoon in the coastal region (Table 5). The TP ranged from 35.97 ± 9.94 μM (winter) to 48.25 ± 13.40 μM (post-monsoon) in the creek, 17 ± 7.07 μM (summer) to 20.40 ± 1.34 μM during (winter) in the upstream, 23.16 ± 4.60 μM (summer) to 33.19 ± 7.25 μM (post-monsoon) in the estuary and 14.20 ± 3.25 μM (post-monsoon) to 22.58 ± 11.20 μM (winter) in the coastal water, respectively, in 2011. However in 2012, it was recorded between 41.86 ± 7.21 μM (winter) to 70.11 ± 12.77 μM (monsoon) in the creek, 12.62 ± 2.31 μM (summer) to 16.61 ± 0.52 μM (winter) in the upstream, 29.34 ± 4.56 μM

(winter) to 43.94 ± 7.68 μM (post-monsoon) in the estuary and 14.34 ± 5 μM (summer) to 24.94 ± 7.92 μM (post-monsoon) in the coastal.

The spatial variation of silicate in all regions is presented in Fig. 4. The distribution of the Silicate (SiO₄-Si) in the study area ranged from 24 ± 2.16 μM (post-monsoon) to 47.55 ± 3.30 μM (monsoon), from 18.50 ± 0.71 μM (summer) to 65.50 ± 0.71 μM (monsoon), from 21.73 ± 9.61 μM (post-monsoon) to 39.19 ± 21.12 μM (monsoon) and from 11.96 ± 10.91 μM (post-monsoon) to 27.33 ± 12.19 μM (monsoon) in the creek, upstream, estuary and coastal water of Mahanadi, respectively, during 2011 (Table 3, Fig. 4). On the other hand in 2012, the concentration of silicate in creek, upstream and estuary ranged from 94.32 ± 21.61 μM, 153.78 ± 12.08 μM and 94.32 ± 21.61 μM, respectively, during monsoon and 50.16 ± 20.34 μM, 21.22 ± 1.29 μM and 50.16 ± 20.34 μM during summer, respectively. In the coastal waters, it varied from 9.88 ± 4.20 μM during summer to 46.35 ± 18.52 μM during monsoon (Table 5).

The higher concentration of chlorophyll-*a* (Chl-*a*) was recorded from the creek (11.50 ± 3.70 mg m⁻³) and upstream



Table 4 Seasonal and spatial distribution of nutrients (μM) and Chlorophyll-*a* (mg m^{-3}) along the study region during 2011

Parameter	Season Sector	Summer	Monsoon	Post-monsoon	Winter
		Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
NO ₂ -N	Creek	2.50 \pm 1.73	9.75 \pm 1.71	5.25 \pm 3.77	3.91 \pm 1.36
	River	0.67 \pm 0.03	4.00 \pm 0.04	1.00 \pm 0.07	0.85 \pm 0.01
	Estuary	0.31 \pm 0.22	2.83 \pm 1.17	1.06 \pm 0.39	0.99 \pm 0.29
	Coastal	0.16 \pm 0.24	1.71 \pm 0.78	0.51 \pm 0.33	0.50 \pm 0.49
NO ₃ -N	Creek	15.25 \pm 4.57	65.50 \pm 36.45	33.00 \pm 12.54	20.56 \pm 7.32
	River	2.00 \pm 0.05	11.00 \pm 1.41	8.00 \pm 0.07	5.84 \pm 0.68
	Estuary	3.08 \pm 2.06	11.59 \pm 5.93	9.92 \pm 4.95	6.43 \pm 3.33
	Coastal	2.28 \pm 1.22	3.07 \pm 2.79	3.13 \pm 3.04	4.19 \pm 2.61
NH ₄ ⁺	Creek	10.00 \pm 4.24	43.50 \pm 21.46	20.50 \pm 8.35	19.53 \pm 7.46
	River	1.00 \pm 0.02	10.00 \pm 0.01	10.00 \pm 0.01	5.35 \pm 0.01
	Estuary	4.06 \pm 2.22	17.37 \pm 7.31	10.30 \pm 4.19	5.11 \pm 3.10
	Coastal	2.37 \pm 1.56	11.39 \pm 7.50	1.33 \pm 0.94	3.84 \pm 3.26
TN	Creek	70.00 \pm 37.42	156.50 \pm 71.22	89.25 \pm 10.72	67.98 \pm 23.90
	River	21.00 \pm 0.04	58.00 \pm 1.41	65.50 \pm 0.71	37.28 \pm 2.89
	Estuary	31.24 \pm 8.82	62.82 \pm 19.03	61.47 \pm 17.10	38.63 \pm 13.27
	Coastal	29.28 \pm 13.54	42.46 \pm 23.24	38.49 \pm 9.32	38.58 \pm 7.85
PO ₄ -P	Creek	36.25 \pm 14.80	38.50 \pm 14.66	39.75 \pm 10.63	29.63 \pm 10.85
	River	12.00 \pm 1.41	13.50 \pm 2.12	13.00 \pm 1.41	11.28 \pm 0.08
	Estuary	15.77 \pm 4.06	19.22 \pm 3.61	24.06 \pm 7.23	20.49 \pm 6.15
	Coastal	10.93 \pm 5.16	11.74 \pm 5.70	10.47 \pm 7.47	12.84 \pm 7.70
TP μM	Creek	45.00 \pm 13.59	46.75 \pm 18.23	48.25 \pm 13.40	35.47 \pm 9.94
	River	17.00 \pm 7.07	18.00 \pm 5.66	19.00 \pm 5.66	20.40 \pm 1.34
	Estuary	23.16 \pm 4.60	28.69 \pm 3.45	33.19 \pm 7.25	31.25 \pm 5.81
	Coastal	17.95 \pm 4.59	16.37 \pm 8.51	14.20 \pm 8.15	22.56 \pm 11.20
SiO ₄ -Si	Creek	29.50 \pm 14.57	47.25 \pm 3.30	24.00 \pm 2.16	36.50 \pm 3.70
	River	18.50 \pm 0.71	65.50 \pm 0.71	32.50 \pm 0.71	45.50 \pm 0.71
	Estuary	34.63 \pm 11.79	39.19 \pm 21.12	21.73 \pm 9.16	32.75 \pm 13.60
	Coastal	15.85 \pm 12.90	19.87 \pm 16.43	11.96 \pm 10.91	27.33 \pm 12.19
Chlorophyll- <i>a</i>	Creek	11.50 \pm 3.70	8.50 \pm 2.65	9.25 \pm 3.77	8.25 \pm 2.22
	River	5.00 \pm 1.41	3.50 \pm 0.71	3.50 \pm 0.71	3.50 \pm 0.71
	Estuary	3.25 \pm 0.96	2.75 \pm 0.50	5.50 \pm 1.73	4.75 \pm 1.71
	Coastal	4.33 \pm 3.01	3.50 \pm 3.33	4.00 \pm 4.00	3.67 \pm 3.88

(5 \pm 1.41 mg m^{-3}) during summer and lower values such as 8.25 \pm 2.22 mg m^{-3} and 3.50 \pm 0.71 mg m^{-3} , respectively, recorded in winter during 2011. In the estuary and in the coastal waters, it varied from 2.75 \pm 0.50 mg m^{-3} in monsoon to 5.50 \pm 1.73 mg m^{-3} in post-monsoon while it varied from 3.50 \pm 3.33 mg m^{-3} in monsoon to 4.33 \pm 3.01 mg m^{-3} in summer. Similarly the distribution of silicate in creek and upstream ranged from 7.50 \pm 2.26 mg m^{-3} and 3.50 \pm 0.57 mg m^{-3} in winter to 12.91 \pm 4.50 mg m^{-3} and 6.75 \pm 1.34 mg m^{-3} in summer, respectively, during 2012. In estuary and the coastal waters, it varied from 3.70 \pm 0.54 mg m^{-3} and 3.87 \pm 3.03 mg m^{-3} in summer to 4.85 \pm 2.54 mg m^{-3} and 4.28 \pm 4.35 mg m^{-3} in post-monsoon along the study area during 2012.

The concentrations of dissolved inorganic nitrogen (DIN = NO₂ + NO₃ + NH₄) ranged between 21.51 to 179.87 μM for creek, 2.52 to 37.64 μM for upstream, 3.44

to 67.97 μM for estuary and 1.8 to 30.38 μM in coastal water during 2011 and 2012, respectively (Table 6). Dissolved organic nitrogen (DON = TN-DIN) varied from 9.31 to 103.11 μM , 8.03 to 48.58 μM , 8.03 to 89.20 μM and 8.96 to 81.62 μM for creek, upstream, estuary and coastal area, respectively, during 2011 and 2012 (Table 6). The spatial and seasonal variation of total phosphorus and (DOP = TP-DIP) showed similar trend as in case of inorganic phosphate. The higher concentrations of DOP (59.63 μM) and TP (77.42 μM) were found in creek in all seasons (Table 6 and Fig. 4). The N:P ratio of Mahanadi river estuarine system varied between 0.45 to 3.43 for creek, 0.27 to 2.02 for upstream, 0.20 to 2.51 for estuary and 0.23 to 1.63 in coastal surface water (Table 7) and the Si:P ratio varied between 11.80 to 93.59 for creek, 20.25 to 552.64 for upstream, 10.23



Table 5 Seasonal and spatial distribution of nutrients (μM) and chlorophyll-*a* (mg m^{-3}) along the study region during 2012

Parameter	Season Sector	Summer	Monsoon	Post-monsoon	Winter
		Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
NO ₂ -N	Creek	1.79 \pm 0.53	7.59 \pm 1.36	9.38 \pm 1.73	10.89 \pm 3.65
	River	0.89 \pm 0.05	3.94 \pm 0.56	0.93 \pm 0.08	0.36 \pm 0.03
	Estuary	0.51 \pm 0.36	4.76 \pm 3.59	0.94 \pm 0.36	0.92 \pm 0.73
	Coastal	0.18 \pm 0.08	1.27 \pm 0.42	0.61 \pm 0.40	0.36 \pm 0.22
NO ₃ -N	Creek	24.13 \pm 14.10	58.83 \pm 23.76	68.77 \pm 30.35	61.48 \pm 43.21
	River	2.18 \pm 0.24	21.05 \pm 3.22	2.40 \pm 0.39	1.05 \pm 0.39
	Estuary	5.64 \pm 0.67	18.31 \pm 10.93	8.16 \pm 5.06	3.61 \pm 2.21
	Coastal	3.48 \pm 1.44	10.14 \pm 5.71	4.17 \pm 0.90	2.39 \pm 0.60
NH ₄ ⁺	Creek	15.12 \pm 6.50	38.55 \pm 27.62	42.63 \pm 26.42	36.51 \pm 26.24
	River	1.57 \pm 0.78	10.61 \pm 0.88	2.80 \pm 0.25	1.52 \pm 0.05
	Estuary	5.19 \pm 1.63	14.08 \pm 8.43	6.92 \pm 1.86	3.86 \pm 4.06
	Coastal	2.27 \pm 1.20	5.87 \pm 4.40	3.67 \pm 2.73	2.09 \pm 0.85
TN	Creek	80.48 \pm 16.83	166.51 \pm 89.48	168.30 \pm 67.19	170.12 \pm 95.33
	River	33.19 \pm 4.15	46.78 \pm 1.56	50.23 \pm 7.04	43.00 \pm 8.16
	Estuary	40.14 \pm 3.67	77.11 \pm 21.04	62.97 \pm 21.65	78.88 \pm 15.32
	Coastal	22.84 \pm 5.32	36.61 \pm 14.75	57.86 \pm 21.79	46.66 \pm 21.07
PO ₄ -P	Creek	31.45 \pm 11.19	48.08 \pm 10.64	48.12 \pm 13.49	26.61 \pm 11.51
	River	6.54 \pm 1.95	13.21 \pm 2.83	11.35 \pm 2.65	9.93 \pm 1.68
	Estuary	16.94 \pm 5.00	23.63 \pm 4.51	28.34 \pm 4.88	16.31 \pm 4.80
	Coastal	8.72 \pm 5.49	11.36 \pm 4.53	16.02 \pm 5.95	11.24 \pm 5.25
TP	Creek	46.97 \pm 9.28	70.11 \pm 12.37	57.98 \pm 8.26	41.86 \pm 7.21
	River	12.62 \pm 2.21	21.67 \pm 0.79	15.08 \pm 5.38	16.61 \pm 0.52
	Estuary	32.57 \pm 5.14	30.07 \pm 5.10	43.94 \pm 7.68	29.34 \pm 4.56
	Coastal	14.34 \pm 5.00	16.24 \pm 6.26	24.94 \pm 7.92	21.53 \pm 12.03
SiO ₄ -Si	Creek	50.16 \pm 20.34	65.86 \pm 21.70	60.15 \pm 17.49	94.32 \pm 21.69
	River	21.22 \pm 1.29	98.65 \pm 0.61	49.64 \pm 2.10	153.78 \pm 12.08
	Estuary	12.66 \pm 3.39	81.64 \pm 22.02	33.31 \pm 8.38	110.80 \pm 26.71
	Coastal	9.88 \pm 4.20	46.35 \pm 18.52	18.29 \pm 12.00	29.14 \pm 29.49
Chlorophyll- <i>a</i>	Creek	12.91 \pm 4.50	9.71 \pm 3.50	8.53 \pm 3.13	7.50 \pm 2.26
	River	6.75 \pm 1.34	3.65 \pm 0.64	4.15 \pm 0.49	3.50 \pm 0.57
	Estuary	3.70 \pm 0.54	3.30 \pm 0.83	4.85 \pm 2.54	4.13 \pm 1.61
	Coastal	3.87 \pm 3.03	3.90 \pm 3.22	4.28 \pm 4.35	4.07 \pm 3.82

to 524.69 for estuary and 4.52 to 313.67 in coastal surface water during 2011 and 2012, respectively (Table 7).

Multivariate statistical techniques

The correlation coefficients with their level of significance of parameters in surface water of the estuarine coastal ecosystem are presented in Table 8. It was found that salinity has significant positive correlation with DO ($r=0.720$) and negative correlation with TSS ($r=-0.803$), BOD ($r=-0.731$), NO₂ ($r=-0.666$), NO₃ ($r=-0.570$), NH₄⁺ ($r=-0.684$), TN ($r=-0.676$), PO₄ ($r=-0.513$), TP ($r=-0.461$), SiO₄ ($r=-0.475$), and Chl-*a* ($r=-0.330$). The Chl-*a* have strong positive relationship with nutrients NO₂ ($r=0.498$), NO₃ ($r=0.471$), NH₄⁺ ($r=0.432$), TN ($r=0.506$),

PO₄ ($r=0.758$), TP ($r=0.715$) and BOD ($r=0.541$), whereas a negative correlation with DO showed ($r=-0.548$), pH ($r=-0.582$) and salinity ($r=-0.330$). The factor analysis showed that there are three factors having eigenvalues more than one which is accounting 80.43% of the total variance with the 16 environment variables of the study area (Table 6). The Factor-1 contributed for 45.81% of the total variance in the data sets and has a significant positive loadings on BOD, NO₂, NO₃, NH₄, TN, PO₄, TP, Chl-*a* whereas strong negative loading of pH, DO and salinity. The factor-2 contributed for 25.12% of the total variances and significant positive loadings on TSS, NO₂, NO₃, NH₄, TN, SiO₄, and negative loadings with pH, DO and salinity revealed that the river discharge and anthropogenic inputs into the Mahanadi river-estuarine system. The Factor-3 accounting 9.497% of the total variances is negative loading of NO₂ and

Fig. 5 Clustering of the 14 sampling stations along the estuary, Mahanadi River and coastal ecosystem

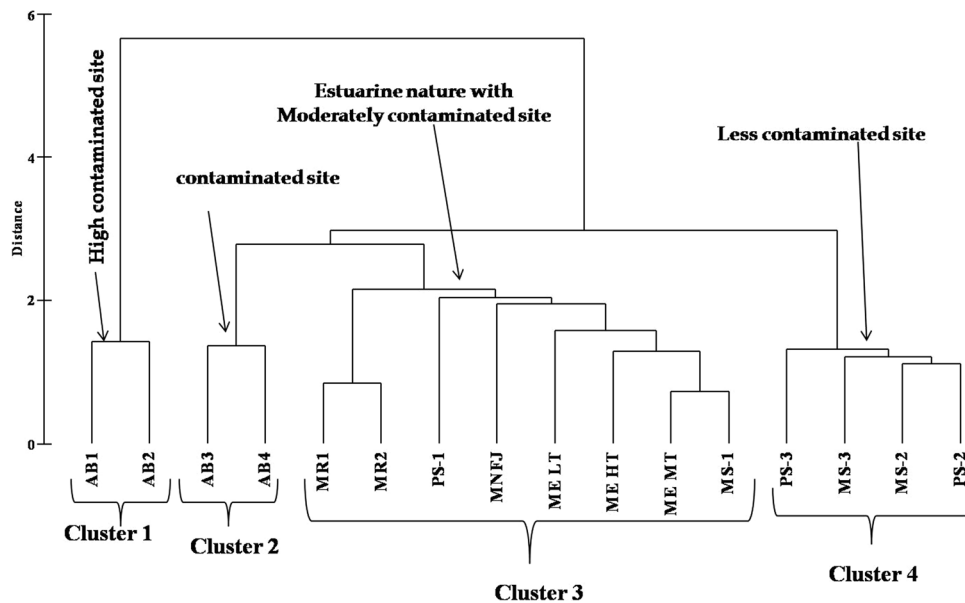


Table 6 Seasonal and temporal variation of Dissolved inorganic and organic nitrogen, phosphorous, Refill ratio during 2011

Parameter	Season Sector	Summer Mean ± SD	Monsoon Mean ± SD	Post-monsoon Mean ± SD	Winter Mean ± SD
DIN μM	Creek	27.99 ± 9.03	119.33 ± 59.08	59.42 ± 23.12	44.00 ± 15.91
	River	3.59 ± 0.06	25.71 ± 1.31	19.46 ± 0.03	12.03 ± 0.66
	Estuary	7.37 ± 3.94	31.88 ± 10.66	21.28 ± 9.24	12.53 ± 6.62
	Coastal	5.10 ± 2.61	16.33 ± 9.82	5.03 ± 4.16	8.47 ± 6.22
DON μM	Creek	42.24 ± 33.56	37.48 ± 12.74	29.87 ± 13.13	23.98 ± 11.51
	River	17.67 ± .01	32.57 ± 0.17	46.37 ± 0.69	25.25 ± 2.23
	Estuary	23.93 ± 6.24	31.00 ± 15.34	40.24 ± 9.55	26.11 ± 7.74
	Coastal	24.22 ± 10.89	26.29 ± 14.07	33.46 ± 6.13	30.20 ± 7.81
DOP μM	Creek	9.03 ± 1.74	8.36 ± 4.67	48.24 ± 13.42	5.84 ± 1.89
	River	5.01 ± 5.65	4.44 ± 3.49	19.34 ± 5.81	9.12 ± 1.26
	Estuary	7.53 ± 1.25	9.36 ± 0.68	33.10 ± 7.31	10.76 ± 1.60
	Coastal	6.94 ± 3.19	4.78 ± 3.40	14.26 ± 8.15	9.81 ± 4.01
N:P	Creek	0.85 ± 0.28	3.00 ± 0.52	1.46 ± 0.26	1.52 ± 0.41
	River	0.29 ± 0.03	1.89 ± 0.19	1.51 ± 0.11	1.07 ± 0.05
	Estuary	0.47 ± 0.23	1.68 ± 0.60	0.92 ± 0.49	0.70 ± 0.46
	Coastal	0.51 ± 0.32	1.33 ± 0.27	0.48 ± 0.08	0.74 ± 0.35
N:P:Si	Creek	44.21 ± 36.65	16.43 ± 4.54	17.14 ± 4.36	25.57 ± 8.51
	River	63.17 ± 9.15	35.09 ± 4.02	21.76 ± 2.14	43.04 ± 1.40
	Estuary	90.86 ± 48.70	26.71 ± 17.83	26.41 ± 11.08	68.51 ± 47.08
	Coastal	38.85 ± 33.09	14.71 ± 10.31	24.85 ± 19.97	44.82 ± 22.75

positive loading of WT. The dendrogram obtained from the cluster analysis and classified the entire region into three different hydrological groups (Fig. 5). During the study period, the Cluster-1 is represented by the creek stations AB1 and AB2; Cluster-2 represented three subgroup 2A, 2B and 2C. The subgroup 2A represented by creek stations in (AB3 and AB4), 2B denoted as upstream stations (MR1 and MR2) and 2C corresponds to estuarine nature regions

(MNFJ, ME, MS1 and PS1) while Cluster-3 corresponds to coastal water (MS-2, MS-3, PS-2 and PS-3). The regression analysis between salinity and nutrients (Fig. 6) shows that there is a negative correlation exists between salinity and nutrients and the correlation values (r) ranged between 0.17 and 0.39 (Table 9).

Table 7 Seasonal and temporal variation of Dissolved inorganic and organic nitrogen, phosphorous, Redfill ratio during 2012

Parameter	Season Sector	Summer	Monsoon	Post-monsoon	Winter
		Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
DIN μ M	Creek	41.04 \pm 21.01	119.33 \pm 59.08	59.42 \pm 23.12	67.98 \pm 23.90
	River	4.64 \pm 1.07	25.71 \pm 1.31	19.46 \pm 0.03	37.28 \pm 2.89
	Estuary	11.34 \pm 2.50	31.88 \pm 10.66	21.28 \pm 9.24	38.63 \pm 13.27
	Coastal	5.94 \pm 2.67	16.33 \pm 9.82	5.03 \pm 4.16	38.68 \pm 7.89
DON μ M	Creek	39.44 \pm 12.91	61.55 \pm 38.49	46.70 \pm 23.39	61.24 \pm 23.48
	River	28.55 \pm 3.08	11.19 \pm 4.46	44.79 \pm 7.28	40.08 \pm 7.67
	Estuary	28.79 \pm 4.12	39.97 \pm 21.52	42.68 \pm 9.16	70.49 \pm 18.27
	Coastal	16.90 \pm 3.04	19.34 \pm 6.89	53.72 \pm 19.47	41.82 \pm 20.24
DOP μ M	Creek	15.52 \pm 4.45	22.04 \pm 7.09	7.15 \pm 1.84	15.24 \pm 5.06
	River	6.08 \pm 0.25	8.46 \pm 2.04	9.90 \pm 11.46	6.68 \pm 1.16
	Estuary	15.63 \pm 5.00	6.43 \pm 1.58	12.36 \pm 10.16	13.03 \pm 3.13
	Coastal	5.62 \pm 2.39	4.88 \pm 3.13	11.04 \pm 4.31	10.29 \pm 7.20
N:P	Creek	1.25 \pm 0.23	2.08 \pm 0.62	2.52 \pm 0.70	3.90 \pm 1.41
	River	0.72 \pm 0.05	2.78 \pm 0.82	1.37 \pm 1.09	0.29 \pm 0.00
	Estuary	0.68 \pm 0.07	1.61 \pm 0.92	0.47 \pm 0.05	0.52 \pm 0.43
	Coastal	0.76 \pm 0.19	1.52 \pm 0.57	0.58 \pm 0.15	0.47 \pm 0.15
N:P:Si	Creek	39.29 \pm 10.97	31.43 \pm 3.04	27.01 \pm 2.51	26.43 \pm 9.42
	River	29.64 \pm 0.29	37.09 \pm 11.09	52.53 \pm 47.75	522.25 \pm 42.98
	Estuary	19.01 \pm 6.69	71.99 \pm 49.30	72.36 \pm 19.47	313.67 \pm 187.51
	Coastal	14.72 \pm 9.64	35.36 \pm 18.07	40.19 \pm 19.35	84.27 \pm 114.22

Water quality Index (WQI)

The water quality index is a number without units that indicates the overall quality of surface water by taking into account all observed water variables. In other words, the WQI evaluation method converts a series of data (chemical, physical, and biological factors) into a single value (0–100) and then categorizing the water quality considering the significance poor to an excellent (Meher et al. 2018; Zhao et al. 2020). The standard Canadian Council of Ministers of the Environment CCME-WQI was derived integrating the multiple water variables gathered from the four sites throughout the research period to completely analyze the water quality. During the research period, the water quality index (CCME INDEX) of the Canadian Council of Ministers of the Environment (CCME) indicated an increasing trend in coastal water (25.66) followed by the estuary (17.86), river (17.14), and (16.85) creek (Table 10; Fig. 7). As a result, it is evident that the surface water quality in the Mahanadi estuarine and coastal habitat predominantly impacted by effluents discharge from industrial, river, and agriculture runoff, and anthropogenic activities in the upstream and creek regions (Zhao et al. 2020).

Discussions

A seasonality variation was showed a strong influence on water temperature in the study period. The distinction of temperature between years was negligible, but between seasons was prominent. The tropical estuary consistently showed a high temperature condition throughout of the year (Costa et al. 2017). The results indicate the dissolving of gases such as oxygen in water reducing their availability for biological and chemical activities (Wu et al. 2016). Among the abiotic factors, the recorded pH is showed an acidic to slightly alkaline condition with a low average value recorded (6.61 ± 0.68) for creek and was maximum (8.12 ± 0.10) for the coastal region during the study period. The higher pH value was observed at the coastal water because of the inundation of water in the region while the lower pH was at the creek, might be the ascendancy of acidic effluents released from the fertilizer industries in Paradip. An earlier study has been revealed that the pH of Mahanadi region was strongly impacted by the seawater and acidic industrial effluents (Panda et al. 2006; Sundaray et al. 2006, 2009; Khadanga et al. 2012).

The estuarine gradient was characterized by differences in the salinity in the region. The average lower value of salinity was found (3.63 ± 0.43) in upstream during monsoon and higher in coastal water (28.30 ± 2.70) during pre-monsoon. The salinity showed a decreasing trend from summer to monsoon and was insignificant increasing in winter season

Table 8 Correlation matrix of physico-chemical and biological parameters in the study area

	WT	TSS	pH	Sal	DO	BOD	NO ₂ -N	NO ₃ -N	NH ₄ ⁺	TN	PO ₄ -P	TP	SiO ₄ -Si	Chl- <i>a</i>
WT	1													
TSS	-0.0323**	1												
pH	0.132	-0.263*	1											
Sal	0.184	-0.803**	0.502**	1										
DO	0.241	-0.594**	0.763**	0.720**	1									
BOD	-0.176	0.589**	-0.760**	-0.731**	-0.901**	1								
NO ₂ -N	-0.328**	0.579**	-0.748**	-0.666**	-0.878**	0.843**	1							
NO ₃ -N	-0.187	0.529**	-0.642**	-0.570**	-0.846**	0.798**	0.886**	1						
NH ₄ ⁺	-0.242	0.640**	-0.669**	-0.684**	-0.882**	0.859**	0.871**	0.924**	1					
TN	-0.143	0.636**	-0.635**	-0.676**	-0.853**	0.798**	0.834**	0.925**	0.929**	1				
PO ₄ -P	-0.082	0.379**	-0.632**	-0.513**	-0.766**	0.761**	0.724**	0.742**	0.723**	0.795**	1			
TP	-0.130	0.360**	-0.570**	-0.461**	-0.715**	0.716**	0.684**	0.729**	0.709**	0.774**	0.974**	1		
SiO ₄ -Si	-0.195	0.464**	-0.467**	-0.475**	-0.403**	0.433**	0.418**	0.324**	0.416**	0.443**	0.399**	0.415**	1	
Chl- <i>a</i>	0.090	0.180	-0.482**	-0.330**	-0.548**	0.541**	0.498**	0.471**	0.432**	0.506**	0.758**	0.715**	0.206	1

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

in all stations (Fig. 3). Lower salinities were observed in the creek and upstream during monsoon due to the influx of fresh water discharges. Water temperature and salinity were essential factors played a key effect in spreading of the aquatic biota and the development of eco-clines (Dolbeth et al. 2016). The river discharge and rainfall influence on salinity was wide-ranging in the estuary and was regulated by fresh water during monsoon (Sadhuramet al. 2005; Pradhan et al. 2009). During monsoon in 2011, the average lower value of DO with associated the lowest value (0.76 mg L⁻¹) observed in the creek region; however, the lower could be observed sporadically due to anthropic intervention. During the summer, the creek (Atharabanki) of Mahanadi River had the lowest DO of 4.8 mg L⁻¹ and was attributed to organic waste from Paradip township and effluents from fertilizer industries (Samantray et al. 2009); the significantly lower DO value was reported, suggested that the regions of water quality was deteriorated further. A similar condition has been observed as hypoxic for estuarine settings when dissolved oxygen value (≤ 3 mg L⁻¹) elsewhere (Conselho Nacional de Meio Ambiente, 2005). The worldwide literature results were observed as a basis for this investigation, which has been adopted more conservative value (<2 mg L⁻¹) and the limit for hypoxia (Roselli et al. 2009). A few incidences of hypoxia in this study also been observed mostly during the monsoon season, in the estuary's stream. However, this process has been occurred through the balance between production, and consumption (respiration and other chemical processes), and an exchange with the environmental governs that has been resulted DO concentrations in surface waters of the study location (Uriarte and Villate 2004). This decline renewal was resulted in virtually and completes the consumption of available oxygen in water; furthermore, a lesser flow of water caused in low turbulence, resulted in less diffusion from the atmosphere, resulted in hypoxia condition in the region and hence indicated water quality degradation, leading to habitat deterioration, as seen elsewhere (Qian et al. 2018; Bourgault and Cyr 2015; Costa and Barletta 2016; Jeppesen et al. 2016; Schmidt et al. 2016).

The comparative to the earlier studies, the water of creek was more polluted due to the increase of acidic effluent discharge by fertilizer plant and organic waste form Paradip Township, followed by Mahanadi estuary and coastal water (Pradhan et al. 1998; Nayak et al. 2004; Sundaray et al. 2006). During the present study, the higher value (5.92 ± 2.62 mg L⁻¹) of BOD was recorded during monsoon season probably attributed to the influx of organic sewage from the surrounding township to this water. The Nutrients were found in higher concentration in the creek followed by estuary, river and coastal water in the study period. The nitrite and nitrate values showed relatively lower values during summer and observed that the concentrations of nitrate fivefold higher than that of nitrite. A marked

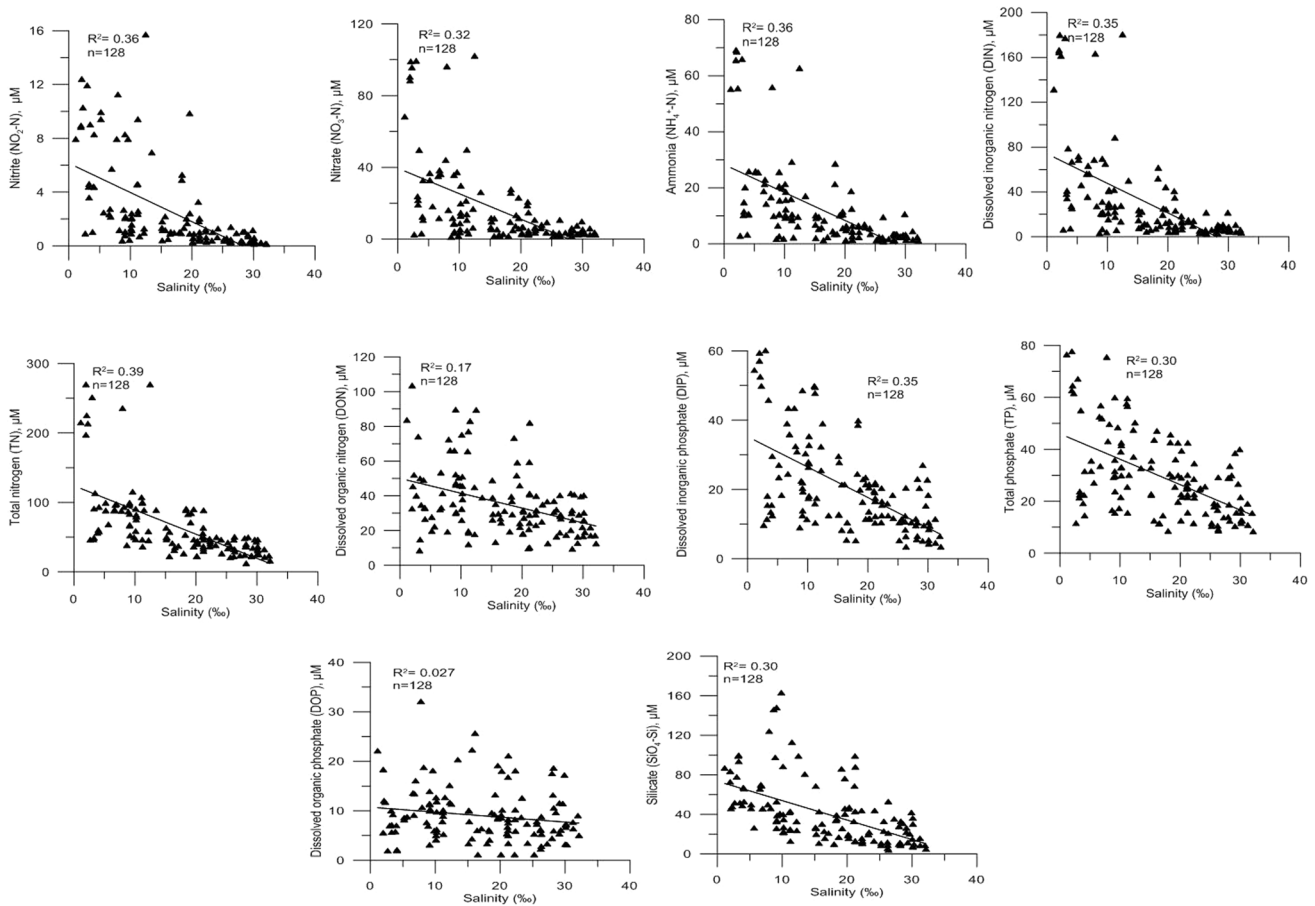


Fig. 6 Linear regression between salinity and nutrient in estuary, Mahanadi River and coastal water ecosystem during the study period

Table 9 Factor loading of water samples in the study area

Parameters	Factor 1	Factor 2	Factor 3
WT	-0.031	-0.107	0.913
TSS	0.173	0.866	-0.230
pH	-0.714	-0.302	0.105
Salinity	-0.350	-0.840	0.068
DO	-0.773	-0.491	0.223
BOD	0.748	0.524	-0.137
NO ₂ -N	0.749	0.453	-0.341
NO ₃ -N	0.790	0.383	-0.257
NH ₄ ⁺	0.724	0.532	-0.273
TN	0.757	0.525	-0.136
PO ₄ -P	0.915	0.224	0.049
TP	0.888	0.195	0.008
SiO ₄ -Si	0.205	0.666	0.043
Chl- <i>a</i>	0.802	0.014	0.281
Eigen value	6.413	3.516	1.330
Total variance (%)	45.810	25.118	9.497
Cumulative (%)	45.810	70.927	80.425

Table 10 Canadian Council of Ministers of the Environment water quality index (CCME INDEX) variation with sites of the study area

Sites	F1 (scope)	F2 (frequency)	F3 (amplitude)	CCME WQI
Creek	80	67.51	98.92	16.85
River	80	70	96.42	17.14
Estuary	80	65	98.07	17.86
Coastal	60	60	96.86	25.66

horizontal gradient in the concentration of these constituents are observed between the regions, indicating that there is a progressive dilution due to the flow of nutrient-rich polluted water from creek to coastal water. The higher concentration of ammonia was found in creek water followed by estuary, upstream and coastal possibly due to its discharge from the organic matter. Lower values of ammonia are observed during summer in this water due to the utilization of phytoplankton as a primary consumer (Naik et al. 2009). The higher value of total nitrogen is observed in the creek compared to other regions are attributed to effluent load from fertilizer plants like PPL and sewage from Paradip Port Township

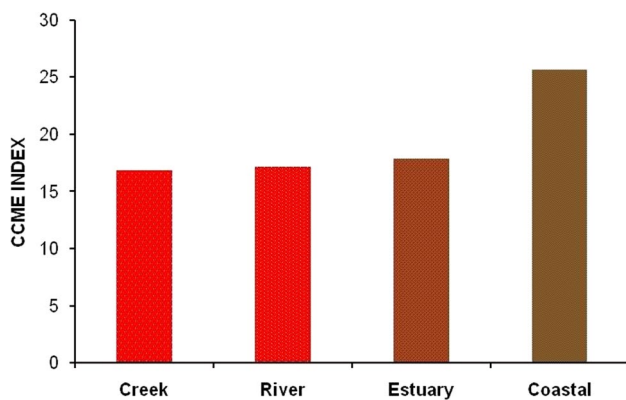


Fig. 7 Water quality index variations in different region of the study area during 2011 and 2012

situated on the upstream of the creek (Panda et al. 2006). Lower concentration of inorganic phosphate is observed in all stations in summer and winter due to high density of phytoplankton and phosphate utilizations (Naik et al. 2009). The spatial and seasonal variation of total phosphorus and DOP shows the similar trend like of inorganic phosphate, TP and DOP concentration and gradually decreases from creek to coastal surface water. The DIP, DOP and TP concentrations were higher in 2011 compared to 2012.

Phosphate and total phosphorous concentrations were higher in the river and estuarine system, due to massive receive of effluents from Paradeep Phosphates Ltd. ($3264 \text{ m}^3 \text{ day}^{-1}$), Oswal Fertiliser Ltd. ($4085 \text{ m}^3 \text{ day}^{-1}$) and the East Coast Breweries and Distilleries Ltd., ($376 \text{ m}^3 \text{ day}^{-1}$) as seen in the region (Sundaray et al. 2006). Addition to this regional monsoon and climate change has impacted as a source of materials from sea and atmosphere to the system. Phosphorus-rich conditions in the water column due to desorption from high sediment loads ($154\text{--}661 \text{ mg L}^{-1}$) during monsoon were unique feature of the estuary (Bhattathiri 2001). The seasonally higher values of BOD, TSS, nitrite, nitrate, ammonia, dissolved inorganic and organic nitrogen (DIN and DON), phosphate, dissolved organic phosphate, total nitrogen, and total phosphate were observed during monsoon was attributed the influx of fresh water runoff along with anthropogenic, industrial and agricultural back runoff into the system (Naik et al. 2009; Sarma et al. 2009; Sundaray et al. 2009; Panda et al. 2006; Samantray et al. 2009; Khadanga et al. 2012). To some extent, the higher concentration of silicate was found in river and estuarine system during winter resulting higher biological productivity due to a biological removal of dissolved silicate from adsorption to suspended sediments (De Souza et al. 1981). However, this phenomenon observed in monsoon was a unique, as the biological productivity is minimum during monsoon and eliminate minimum level of silicate. The silicate concentration was almost equal levels in all the stations.

However, its distribution and variation in study region were behaved more or less conservatively (Naik et al. 2009; Pradhan et al. 2009).

The seasonal variation of biological productivity (Chl-*a*) in the Mahanadi River and the estuarine system was higher during summer attributed the availability of light and wind mixing in water column and lower concentrations was during the monsoon due to the presence of high suspended solids along with low light penetration that act as a cofactor (Naik et al. 2009; Godantharaman 2002; Rajasekar et al. 2005). The results indicating that the nutrients were higher in low tide and lower in high tide in the estuarine surface water and found the seasonal variation of nutrients showed the maximum in monsoon followed by post-monsoon winter and summer. In support to this, the nutrients in study region showed the maximum in creek followed by estuary, upstream and coastal waters. The enrichment of nutrients, higher BOD and lower DO were observed in the present ecosystem due to the influence of the inorganic and organic pollution, received effluents from fertilizer industry and anthropogenic sources near the town ship. The several point sources in between Chaumohana to Nehru Bungalow like Atharabanki creek, Kaudia, of present study area and mangrove litter ingress into the estuary and noticed an additional sources of nutrients into the estuary, and hence, the nutrient concentrations were found to be higher in river and estuarine environments.

The N:P ratio was less than 16:1 in the all stations resulted that the bioavailability of nitrogen for the phytoplankton production in the region was lower compared to the phosphate; hence, the growth of phytoplankton was regulated by the limitation of nitrate (Panigrahy et al. 1999; Ratnam et al. 2022). The N/P ratios ≤ 16 and, similarly, a Si/N ratio ≥ 1 suggested that the nitrate as a limiting component in the study region as seen in rivers along with coastal of BoB (Sarma et al. 2010a, b). The N:P ratio was higher found in monsoon whereas Si:N:P ratio found higher in winter because of the input of nitrogen-rich discharge and anthropogenic sources through nonpoint regions was observed in the study area (Choudhury & Bhadury 2015). The N:P ratio was recorded lower in the all stations ($\leq 16:1$) because it was enriched by high P, low N runoff from terrestrial systems and the increase in P and decrease in N:P indicates that N-restriction in primary production (Elser et al. 1990), and denitrification rate and N-fixation proliferation process that occurred through cyanobacteria (Smith 1983; Howarth et al. 2021).

The correlation coefficients results that nutrients were playing a major role in the ecosystem because of inorganic and organic pollution load from terrestrial regions. In addition to this, the factor analysis indicated that the variables were mainly controlled by river agriculture runoff, anthropogenic, and industries effluents nearby port regions (Sundaray et al. 2006; Panda et al. 2006). The cluster analysis (CA) shows that the ecosystem declined the pollution from the

creek to near shore due the magnitude of anthropogenic and organic load. It was assumed that dissolved nutrients (nitrate, phosphate and silicate) behave non-conservatively during estuarine mixing conditions because of their biological uptake and degradation in the water column. However, non-biological processes, such as adsorption–desorption, nitrification–denitrification and sediment–water exchange, might be contributed to their collective effect to the estuaries. These processes are influenced by seasonal variation of several environmental variables such as temperature, transparency, fresh water influx in the estuaries. The water quality index from analyses also resulted the poor quality of water category in the study region and has been impacted the phytoplankton biomass and ecology. Hence, the water quality of Mahanadi river, creek, estuary and costal water was greatly affected by the major pollutants of nutrients, i.e. total nitrogen and total phosphate (Fig. 4). These findings showed that the water quality in the Mahanadi river, estuarine-coastal environment, is deteriorating on a daily basis. According to health card assessment of water quality, the result shows that the Mahanadi River, creek, estuary, and coastal environment come under poor to extremely poor category during the study period. The present result has also supported the consequence that has been observed by the integrated coastal zone management beyond the present study period from 2013 to 2018 (Biswal et al. 2019). Therefore, it is recommended that further attention and needs to be taken into the action to regulate, abatement, and long-term management of the source of nutrients pollution in the watershed and the study region that pollute and impact into the creek, river and alongside of BoB ecosystem.

Conclusion

Different multivariate statistical analysis on physico-chemical parameters showed that the pollution load coming from the upstream and creek was due to high suspended solids and nutrients during the study period. The water temperature and salinity were indicated distinct seasonal and spatial variations in the river, estuarine and coastal regions of the Mahanadi. The lower DO, pH and higher BOD and nutrients were resulted at creek water because of nonpoint sources into the system. Several point sources in the study area influenced by the anthropogenic sources of nutrients load to the estuary, and therefore, nutrient concentrations were found to be higher in the study region. The result has revealed from perceptible negative correlations between nutrients and salinity in the entire study ecosystem, and is dominated by point and nonpoint sources, freshwater flow and agriculture runoff. Higher levels of phosphate and total phosphorus were found in the river and estuarine system, which receives point sources from fertilizer industries such as Paradip Phosphates

Ltd., Oswal Fertilizer Ltd., East Coast Breweries and Distilleries Ltd located in the bank of river. The behavior of nutrients in the study area was signifying non-conventionally due to their advance and decline in the water column along with the biological processes such as adsorption–desorption that were probably linked to their behavior with sedimentary water. The cluster analysis resulted high pollution in the creek water because of the pollution from point and nonpoint sources in creek region was relatively attentive and hence needs to be monitored. The factor analysis on pollution loading shows a strong positive loading of inorganic nutrients with significant negative loading of salinity and pH, which revealed the organic pollution into the ecosystem. The WQI suggested that ecosystem was poor to extreme poor category, due to the physico-chemical parameters which were responsible for water quality lead to organic pollution from domestic waste effluents, municipal sewage and waste disposal and inorganic pollution from industrial effluents, river and agriculture runoff. Consequently, the estuary was vulnerable, causing by acidification and increased pollution level. This resulted alteration of ecosystem in the region that contributed by long-term environmental changes and, ultimately, the resilience of disastrous occurred repeatedly at the regional ecosystem. Therefore, the study needs to be recommended that the proper industrial management and the necessary actions must be taken to safely disposal of industrial and urban waste to the study region that leads a high level of pollutants in the regional ecosystem and Bay of Bengal.

Recommendation

The concentrations and possible consequences of physico-chemical factors on the creek, Mahanadi River, estuary and coastal environment need to be assessed using a multivariate statistical technique and water quality index consistently. It is also confirmed from previous ecological studies that the aquatic habitats of the main channel creek, Mahanadi River and estuary could be improved for biological resource maintenance persistently for the regional coastal ecosystem. The present investigation and WQI results showed that the water quality of study region was hypoxic condition, but was under acceptable criteria. However, these incidences may be interpreted as a warning indication of the sensitivity and susceptibility of the ecosystem with respect to other comparable settings to human intervention. However, measures to mitigate the impacts on aquatic habitats is essential to initiate at an interim monitoring study with an assessment, inventiveness and encompass to the creek, river and estuary region to maintain environmental quality free from pollution to the ecosystem and sustainable management.



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Declarations

Conflict of interest Authors do not have any conflict of interest for submission and publication of this manuscript.

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