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Elucidation of tidal spatial-temporal variation of physico-chemical and nutrient parameters of estuarine water at South Gujarat

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ABSTRACT

In the present study, the four estuaries were selected from the South Gujarat region to appraise the impact of industrial pollution in the estuarine water samples. The study focused on the tidal variation of nutrients, which disclosed that concentrations of NO_2–N, NO_3–N, NH_4–N, TN, and reactive silicates were higher in low-tide whereas pH, salinity, and dissolved oxygen were higher in high-tide water samples. The results of high BOD and low DO expose the anthropogenic inputs in these estuaries during the low-tide. The results of physico-chemical and nutrients parameters of water showed that the pollution level is strongly influenced by tidal and seasonal changes. Pearson's correlation matrix and principal component analysis (PCA) are applied to a hydrological and hydrographical dataset for finding the spatial-temporal variation during the tidal difference. This study suggested that there is an impact of industrial pollution and anthropogenic inputs on the estuarine water of the study area.

Keywords**:** Estuary water, Physico-chemical parameters, Nutrients, Tidal variation, Principal component analysis

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1. INTRODUCTION

Estuaries are important coastal ecosystems, having a confluence of fresh and marine environments that create a salinity gradient from inner to the outer estuary [1]. These prominent zones regulating material fluxes from terrestrial to the ocean [2], which carried river nutrient loads and therefore, it is the most significant for the ecosystem [3]. This zone receives a significant amount of freshwater, particulates, nutrients, dissolved organic matter, suspended matter and contaminants from surface-dwelling, exchange resources and liveliness with the open ocean. Residential, recreational and mechanized developments (such as marinas) are usually located right on the waterfront with supporting structures such as an embankment create the contamination in these ecosystems.

Industrial and anthropogenic interpolations into the estuarine areas resulted in the discharge of partially treated and untreated wastewater into the insubstantial ecosystem. Among these, the discharge from chemical, paper, pharmaceutical, and food product based industries are considered as paramount sources of inorganic, organic pollutants and heavy metals into the water column [4-6]. The inorganic pollutants in seawater corollary from the decomposition of agricultural organic pollutants, which are because of the excess use of nutrients during cultivation [7-11]. This coastal water leads to the eutrophication process, which is the most common impact of human activities, industrial and coastal development [12-14].

Socioeconomic development in South Gujarat and precipitous industrialization led to the emergence of many industries near rivers. These industries are utilizing freshwater according to need and conveniently disposing of the wastewater either into a river or in the estuaries depending upon their locations. The quality of estuarine water is found to deteriorate in the present study area [15]. The rivers of Gujarat are bearing the impact of industrial pollution due to the heavy industrialization, which generates an enormous quantity of toxic and hazardous wastes [16]. The industrial cluster of Vapi GIDC, central effluent treatment plant (CETP) and other GIDC(s) are located in the vicinity of rivers and estuaries in the south Gujarat region. The environment by surroundings is polluted as a result of the discharge of industrial waste. Vapi is an industrial town, which is listed in the world's top 10 polluted cities [17]. The results of Dudani et al. [18] showed the impact of industrial pollution on the estuaries and overall of the health of the mangrove ecosystem.

The main aim of the present study to the assessment of the spatial and temporal variation of physico-chemical parameters, nutrients and anthropogenic inputs in the estuarine regions of south Gujarat.

2. EXPERIMENTAL

2. 1. Material and methods

2. 1. 1. Study area overview

The South Gujarat estuarine habitats situated at 21.6683 – 20.1531 N latitude and 72.5451 – 72.7428 E longitude. Four estuaries of south Gujarat were selected to explore the pollution status of that region (Fig. 1). (1) Varoli estuary: It is located in Umargam and location 20.21163 N and 72.75619 E were selected for sample collection and used as the least polluted zone. (2) Damanganga estuary (20.41241 N and 72.84033 E): The Damanganga River originates from the Sahyadri hills in Maharashtra and ending in the Arabian Sea near Daman. It is considered as one of the most populated areas in the South of Gujarat [19]. Several reports published elsewhere [19-20] indicates the amount of pollution load in this area. (3) Kolak estuary (20.46548 N and 72.8574 E): The Kolak River originates from Saputara hills near Valvari and meets the Arabian Sea. Zingde et al. [21] reported the water quality of the Kolak river way back in the 1980s and suggested high pressures on engineering and anthropogenic activities. (4) Par (20.5341 N and 72.8881 E): The Par originates from Sahyadri hills of Satpura Range, flows towards the west and joins the Arabian Sea.

Figure 1. Sampling locations (1) Varoli (2) Damanganga, (3) Kolak and (4) Par estuaries of South Gujarat, India

2. 1. 2. Methodology

The study carried out for two successive years in three different seasons, i.e. pre-monsoon (May), post-monsoon (November), and winter (March) between May-2015 to April 2017. The estuarine water samples were collected seasonally using 5 L Niskin sampler in low tide and high tide periods. The estuarine water samples were collected and stored as per prevailing protocols. The physico-chemical variables like temperature, pH, salinity, conductivity, and TDS were measured "in situ" by using a portable Cyber-Scan 650; Eutech – Thermo Fisher Scientific, USA. Turbidity was measured in situ by Eutech TN–100 portable turbidity meter with a resolution of 0.01 NTU. APHA [22] was used for the analysis of Dissolved oxygen (DO) and BOD. The nutrients (i.e. NO_2-N, NO_3-N, NH_4-N, PO_4-P, and SiO_4-Si), the samples were filtered through 0.45 μm pore size cellulose nitrate membrane filter and analyzed as per protocols reported by earlier [23-24].

2. 1. 3. Statistical analysis

The statistical analysis was accomplished by using SPSS (version 20.0) software. The relationship between the physico-chemical variables and nutrients can provide important information on the trend of each parameter during the tidal difference [25]. Pearson's correlation coefficients and its significant level were determined in order to understand the spatial-temporal variation of the nutrients and physico-chemical parameters due to tidal variation. The principal component analysis (PCA) is an important factor in analyzing the estuarine water quality behaviors due to tidal variation.

3. RESULTS AND DISCUSSION

The estuarine environment is exposed to various changes in physico-chemical properties due to the continuous mixing of freshwater with marine water. Assessing water quality is very important in determining the quality of the ecosystem [26].

3. 1. Assessment of physico-chemical water quality parameters

pH is known as the key variable in water since many properties, processes and reactions are pH-dependent. In the estuarine water, the pH range was from 7.8 to 8.3 and it is due to the buffering capacity of the seawater [27]. It was reported that pH 5 to 9 is not directly harmful to aquatic life but such changes can make many common pollutants more toxic in nature [28]. The pH of the water was varied from 6.87 to 8.08 during the low tide and was varied from 7.17 to 8.11 during the high-tide. The average values of pH were 7.64 ±0.38, 7.69 ±0.21, 7.54 ±0.25 and 7.54 ±0.15 for the low-tide samples and it was 7.77 ±0.33, 7.64 ±0.21, 7.70 ±0.20 and 7.80 ± 0.24 for high tide water sample in the Varoli, Damanganga, Kolak, and Par respectively (Fig. 2a).

CO_2 uptake by planktons leads to more dissolution of CO_2 that generates carbonic acid [29] in the winter season and hence the pH values were lower in winter as compared to other seasons. The pH showed negative correlation with NO_3–N ($r = -0.631$, $p<0.01$) and TN ($r = -0.493$, $p<0.05$) for the low-tide samples (Table 1) and it also showed negative correlation with NO_3–N ($r = -0.633$, $p<0.01$) for the high-tide samples (Table 2). The pH and NO_3–N has no direct influence, but pH variation may alter the degree of solubility and kinetics of other chemical reactions of oxygen compounds so that, it can release oxygen radicals or reduced form that favors either the oxidized form of nitrogen or the reduced form of nitrogen [30].

Salinity is an indicator of a freshwater inroad into the seawater of estuaries and extrusion of tidal water in the inland water bodies. The average values of salinity in the surface water samples of Varoli, Damanganga, Kolak and Par estuaries were 35.30 ±2.034 (ppt), 22.095

±11.27 (ppt), 21.74 ±4.89 (ppt) and 32.54 ±5.33 (ppt) during low-tide and the average salinity values were 36.46 ±1.429 (ppt), 31.86 ±5.23 (ppt), 34.0 ±2.44 (ppt) and 35.37 ±2.29 (ppt) in high-tide respectively (Fig. 2b). The salinity showed positive correlation with dissolved oxygen (r = 0.491, $p<0.05$), reactive silicate (r = 0.910, $p<0.01$) and it was negatively correlated with BOD (r = –0.608, $p<0.01$), NO_2–N (r = –0.815, $p<0.01$), NO_3–N (r = –0.769, $p<0.01$), NH_4–N (r = –0.456, $p<0.05$), TN (r = –0.822, $p<0.01$) and PO_4–P (r = –0.456, $p<0.05$) in the low-tide water samples (Table 1). The salinity showed a negative correlation with all nutrients except phosphate in high-tide surface water samples (Table 2). The nutrients were negatively correlated with salinity in each season which was in accordance to work done by Iwata et al [31]. The high values of salinity in the low-tide samples in the pre-monsoon seasons is attributed to the removal of freshwater through the evaporation mechanism [32]. The lowest value of salinity was noticed for the post-monsoon season during the low-tide period, which may be due to the fact that a very high influx of freshwater received by the estuary. Similar results have been registered for Cochin estuaries [33] which, validates our observations.

Conductivity is often used as an alternative measure of dissolved solids and it has direct correlation with dissolved solids for a specific body of water. The conductivity was varied from 15.53 to 57.58 mS/cm in the low-tide and 36.11 to 59.86 mS/cm in the high-tide. The average values of conductivity (mS/cm) at Varoli (52.75 ±2.895 mS/cm), Damanganga (35.44 ±15.89 mS/cm), Kolak (34.259 ±7.04 mS/cm) and Par (49.309 ±7.32 mS/cm) respectively in the low-tide samples and it was found at Varoli (54.74 ±2.57 mS/cm), Damanganga (48.643 ±7.57 mS/cm), Kolak (51.407 ±3.36 mS/cm) and Par (53.16 ±3.15 mS/cm) in the high-tide samples respectively (Fig. 2c). The conductivity was positively correlated with DO (r = 0.483, $p<0.05$), negatively correlated with BOD (r = –0.583, $p<0.05$), NO_2–N (r = –0.796, $p<0.01$), NO3–N (r = –0.729, $p<0.01$), NH_4–N (r = –0.480, $p<0.05$), TN (r = –0.794, $p<0.01$), PO_4–P (r = –0.443, $p<0.05$) and silicate (r = –0.917, $p<0.01$) in the low-tide samples. The conductivity showed positive correlation with turbidity (r = 0.450, $p<0.05$) and negatively correlated with NO_2–N (r = –0.567, $p<0.01$), NO_3–N (r = –0.549, $p<0.01$), NH_4–N (r = –0.674, $p<0.01$) TN (r = –0.539, $p<0.01$) and silicates (r = –0.878, $p<0.01$) in the high-tide samples (Table 1 and 2). The negative correlation of conductivity with all nutrients in low-tide and high-tide was in the congruence with the results reported elsewhere [31, 34].

Conductivity is the measurement of the ability of water to the content of dissolved ionic salts in the water. It is often used as an alternative measure of dissolved solids and it has direct correlation with dissolved solids for a specific body of water. The conductivity was varied from 15.53 to 57.58 mS/cm in the low-tide and 36.11 to 59.86 mS/cm in the high-tide. The average values of conductivity (mS/cm) at Varoli (52.75 ±2.895 mS/cm), Damanganga (35.44 ±15.89 mS/cm), Kolak (34.259 ±7.04 mS/cm) and Par (49.309 ±7.32 mS/cm) respectively in the low-tide samples and it was found at Varoli (54.74 ±2.57 mS/cm), Damanganga (48.643 ±7.57 mS/cm), Kolak (51.407 ±3.36 mS/cm) and Par (53.16 ±3.15 mS/cm) in the high-tide samples respectively (Fig. 2c).

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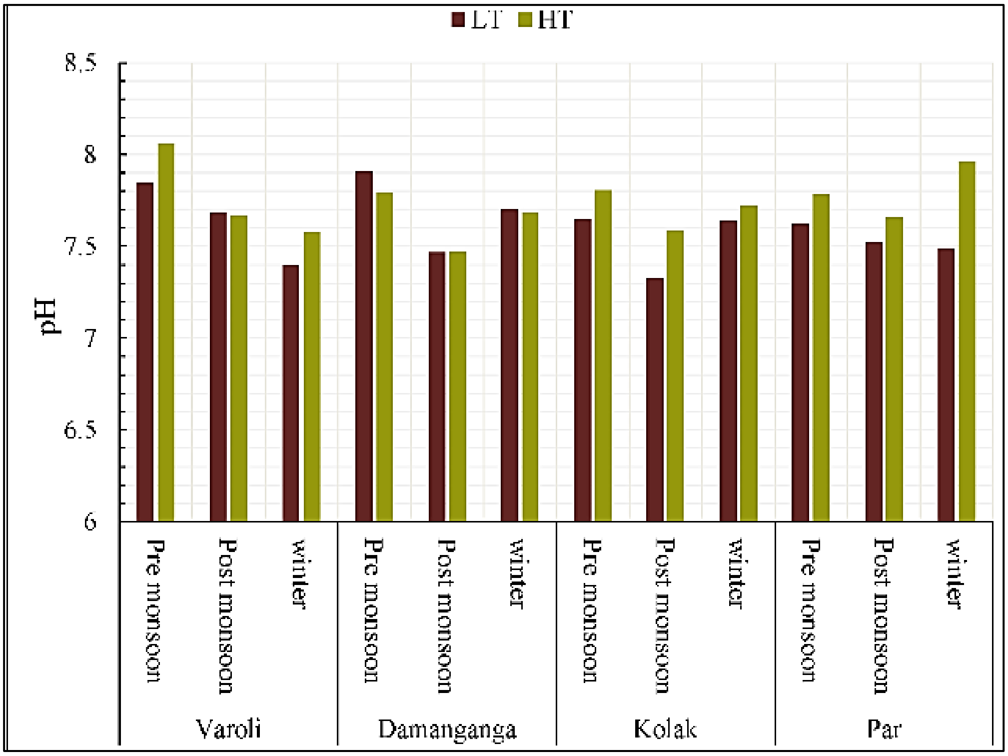
LT
HT
pH
8.5
8
7.5
7
6.5
6
Pre monsoon
Post monsoon
winter
Varoli
Damanganga
Kolak
Par

Fig. 2 (a)

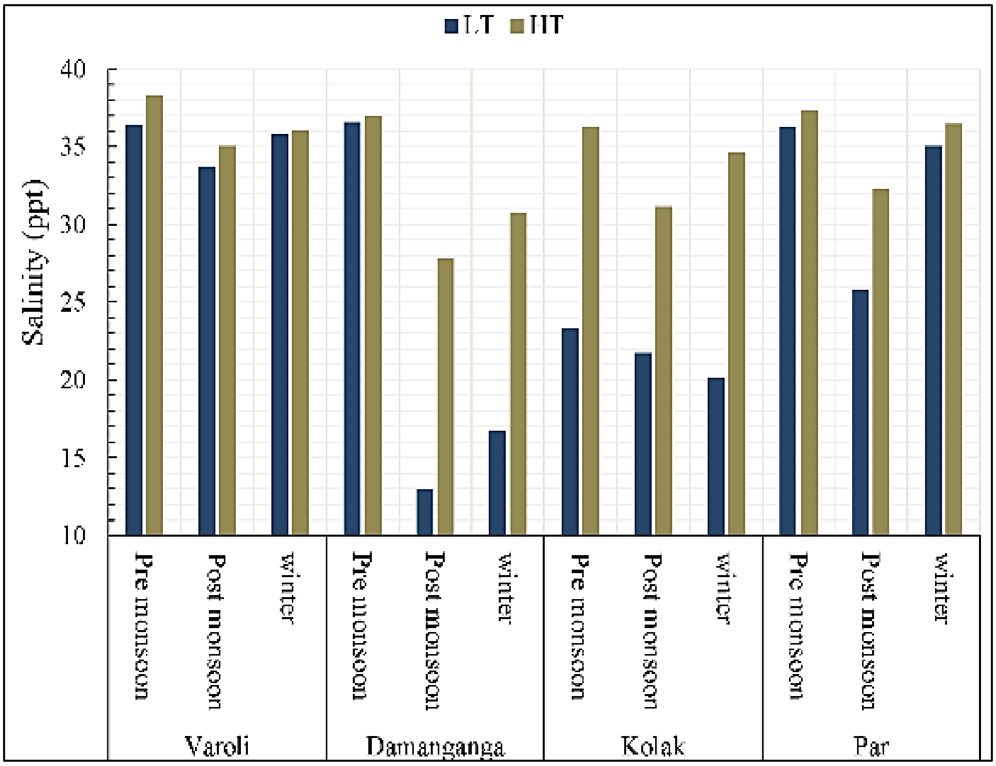
LT
HT
Salinity (ppt)
40
35
30
25
20
15
10
Pre monsoon
Post monsoon
winter
Varoli
Damanganga
Kolak
Par

Fig. 2 (b)

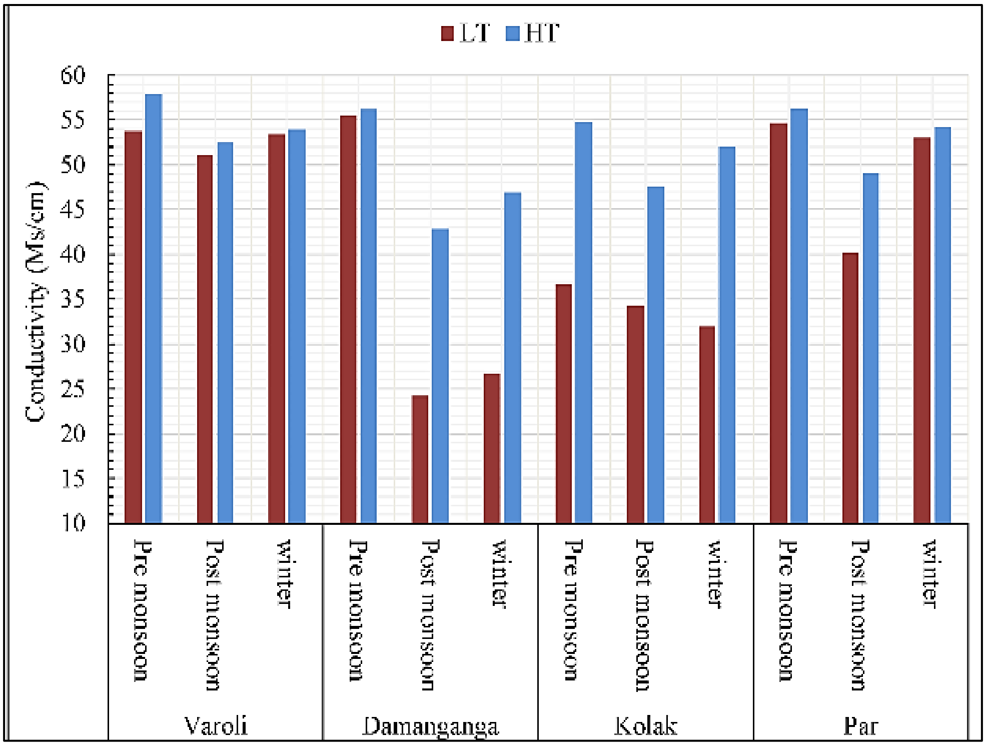
LT
HT
Conductivity (Ms/cm)
60
55
50
45
40
35
30
25
20
15
10
Pre monsoon
Post monsoon
winter
Varoli
Damanganga
Kolak
Par

Fig. 2 (c)

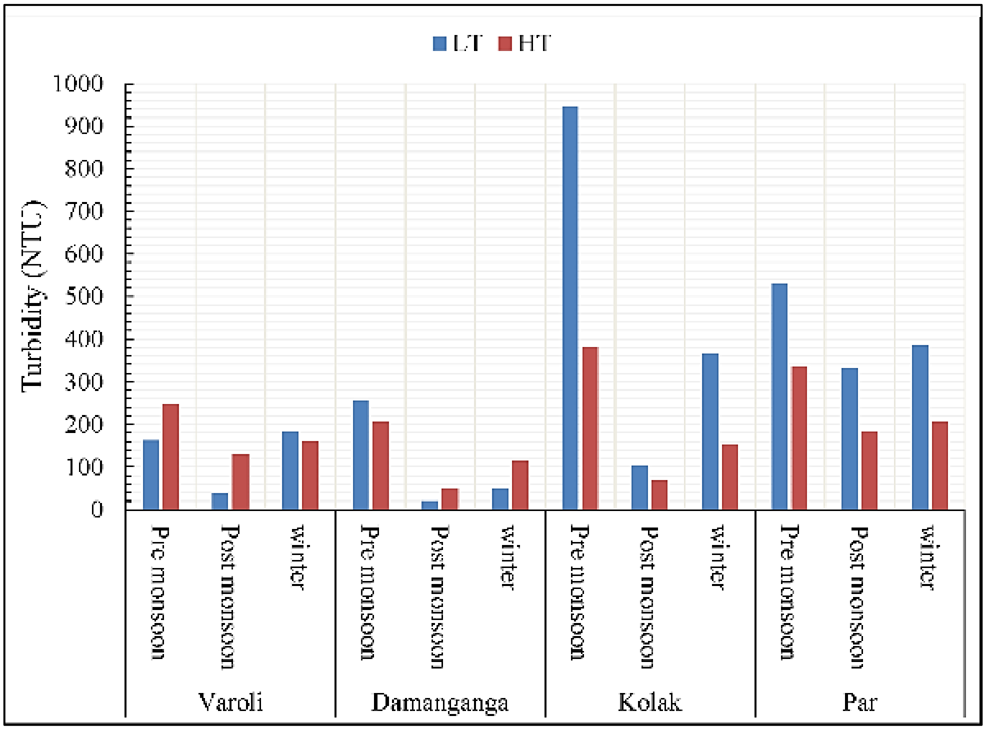
LT
HT
Turbidity (NTU)
1000
900
800
700
600
500
400
300
200
100
0
Pre monsoon
Post monsoon
winter
Varoli
Damanganga
Kolak
Par

Fig. 2 (d)

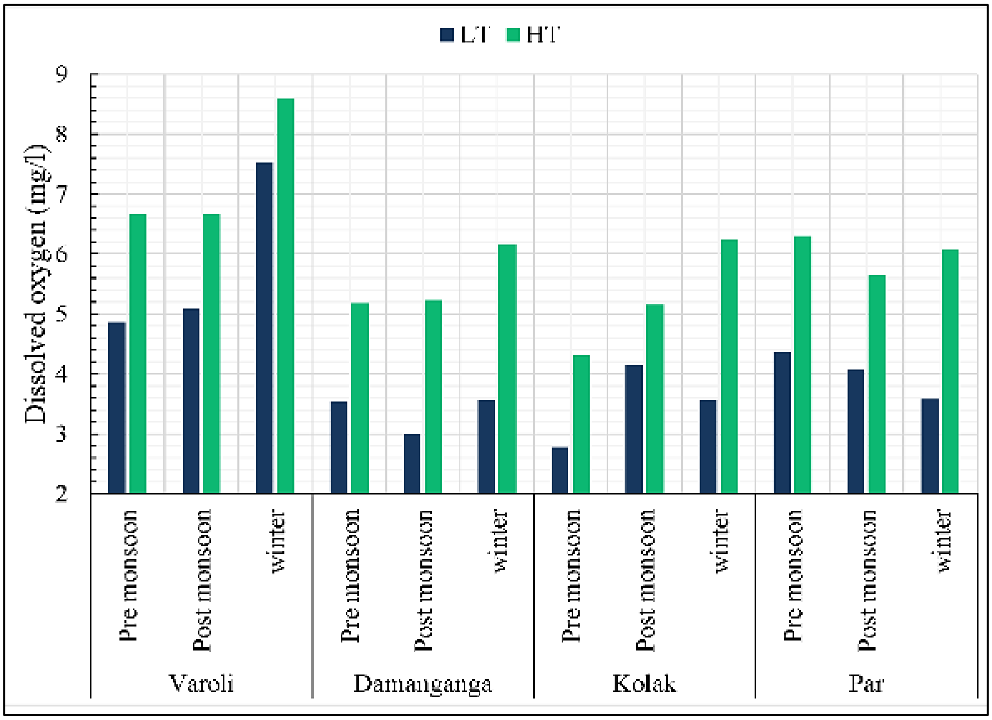

Fig. 2 (e)

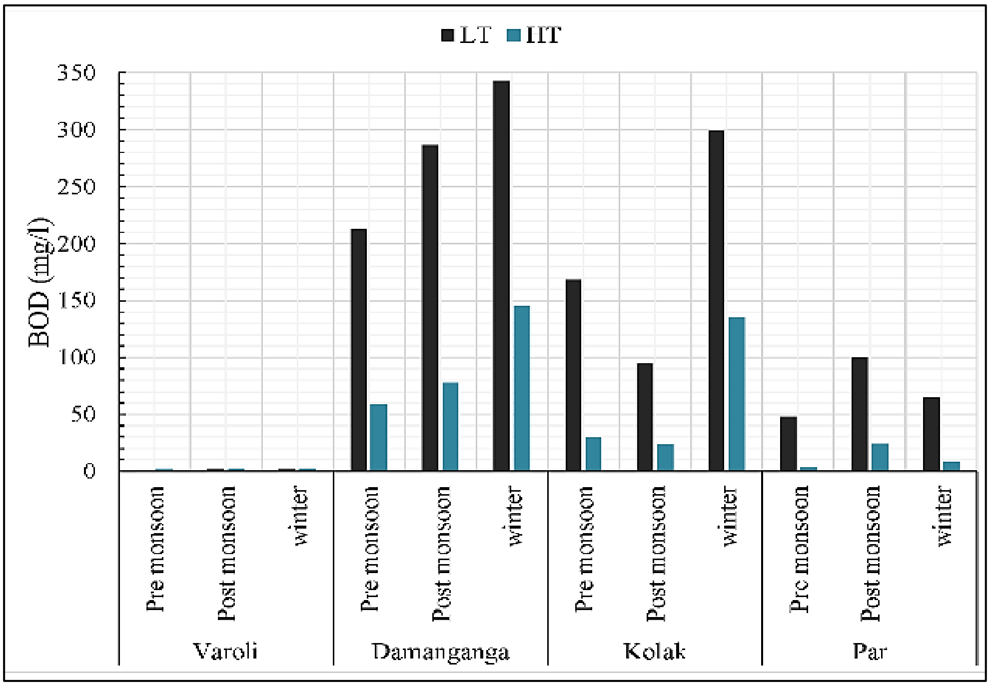

Fig. 2 (f)

Figure 2. Spatial-temporal variation of physico-chemical parameters (2a) pH, (2b) salinity, (2c) conductivity, (2d) turbidity, (2e) DO and (2f) BOD in the surface water during tidal fluctuation at South Gujarat estuaries.

Table 1. Pearson Correlation Matrix for the seawater quality parameter during the low-tide.

Parameter	pH	Salinity	EC	Turbidity	DO	BOD	NO$_2$-N	NO$_3$-N	NH$_4$-N
pH	1	0.180	0.173	-0.036	0.078	0.133	-0.342	-0.631**	-0.016
Salinity		1	0.995**	0.077	0.491*	-0.608**	-0.815**	-0.769**	-0.456*
Conductivity			1	0.068	0.483*	-0.583**	-0.796**	-0.729**	-0.480*
Turbidity				1	-0.371	-0.001	-0.246	-0.337	0.561**
DO					1	-0.473*	-0.404*	-0.432	-0.545*
BOD						1	0.562**	0.456*	0.375
NO$_2$-N							1	0.784**	0.398
NO$_3$-N								1	0.052
NH$_4$-N									1
TN									
Phosphate									
R.silicates									

R.silicates	Phosphate	TN
-0.006	-0.231	-0.493*
0.910**	-0.456*	-0.822**
-0.917**	-0.443*	-0.794**
-0.090	0.133	-0.305
-0.397	-0.478*	-0.421
0.632**	0.497*	0.497*
0.646**	0.495*	0.921**
0.670**	0.449*	0.871**
0.358	0.427	0.281
0.701**	0.436	1
0.473*	1	
1		

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).
Statistical evaluation is done by SPSS (20.0) software

Table 2. Pearson Correlation Matrix for the seawater quality parameter during the high-tide.

DO	Turbidity	EC	Salinity	pH	Parameter
-0.150	0.250	0.282	0.247	1	pH
0.21	0.474*	0.990**	1		Salinity
0.15	0.450*	1			EC
-0.01	1.				Turbidity
1					DO
					BOD
					NO$_2$-N
					NO$_3$-N
					NH$_4$-N
					TN
					Phosphate
					R.silicates

R.silicates	Phosphate	TN	NH_4-N	NO_3-N	NO_2-N	BOD
0.00	-0.28	-0.02	-0.186	-0.633**	-0.208	-0.246
-0.854**	0.06	-0.574**	-0.684**	-0.568**	-0.578**	-0.36
-0.878**	0.08	-0.539**	-0.674**	-0.555*	-0.567**	-0.36
-0.29	0.03	-0.20	-0.557*	-0.41	-0.415*	-0.28
-0.507*	-0.14	-0.37	-0.13	-0.28	-0.17	-0.15
0.33	0.39	0.00	0.16	0.40	0.34	1
0.527*	0.541**	0.721**	0.17	0.824**	1	
0.45	0.607**	0.853**	0.3	1.		
0.43	-0.16	0.21	1			
0.629**	0.39	1				
-0.01	1					
1						

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).
Statistical evaluation is done by SPSS (20.0) software

The negative correlation of conductivity with all nutrients in low-tide and high-tide was in the congruence with the results reported elsewhere [31, 34].

The increasing level of turbidity in the water resulted in the hindrance of penetrating light and this occurrence damaged the aquatic life and also deteriorates the quality of surface water. In the monsoon season, heavy soil erosion and suspended solids from sewage and fresh rainy water increased the turbidity, which has a confrontational effect on the aquatic life [35]. Estuaries are usually more turbid than marine and riverine waters owing to the input of sediment from rivers, the occurrence of dense populations of phytoplankton, and the asset of tidal currents that prevent fine particles to settle down [12]. The Gulf of Khambhat accumulates a heavy inflow of sediments during monsoon season due to the seven major rivers are ending here [36]. The turbidity levels fluctuated from15.9 to 1210 (NTU) during low-tide and 32.4 to 491 (NTU) in high-tide respectively.

The average turbidity in the Varoli (128.31 ±72.48 NTU), Damanganga (108.55 ±107.31 NTU), Kolak (471.5 ±386.86 NTU) and Par (415.43 ±125.68 NTU) during the low-tide and in the high-tide, 179.28 ±137.01 NTU (Varoli), 122.93 ± 69.93 NTU (Damanganga), 200.56 ±149.57 NTU (Kolak) and 240.51 ± 76.17 NTU (Par) respectively (Fig. 2d). The turbidity was positively correlated with NH_4–N ($r = 0.561$, $p<0.01$) during the low-tide and showed negative correlation with NO_2–N ($r = –0.41$, $p<0.05$) and NH_4–N ($r = –0.557$, $p<0.01$) in high-tide samples (Table 1 and 2). The high values of turbidity in the study area during low-tide periods may be attributed to runoff, soil erosion, industrial effluent and muddy flats around estuaries.

Dissolved oxygen (DO) is an important constituent of water and its concentration in water is an indicator of prevailing water quality and the ability of the water body to maintain a judicious aquatic life. The DO divulges the changes that occur in the biological parameters due to the aerobic or anaerobic phenomenon and indicates the condition of the river water for the purpose of the aquatic as well as human life [37]. The DO was varied from 0.648 to 7.78 (mg/L O_2) in the low-tide samples, whereas it was varied between 2.77 to 8.76 (mg/L O_2) in the high-tide samples. The average concentration of DO (mg/L O_2) during the low-tide were 5.83 ±1.32, 3.36 ±0.78, 3.49 ±1.36 and 4.0 ±0.76 and the average values in the high-tide were 6.97 ±1.31, 5.52 ±1.06, 5.23 ±0.88 and 6.01 ±1.06 for Varoli, Damanganga, Kolak and Par estuaries respectively (Fig. 2e).

DO was positively correlated with salinity ($r = 0.491$, $p<0.05$) and was negatively correlated with BOD ($r = –0.473$, $p<0.05$), NO_2–N ($r = –0.404$, $p<0.05$), NO_3–N ($r = –0.432$, $p<0.05$), NH_4–N ($r = –0.545$, $p<0.05$) TN ($r = –0.421$, $p<0.05$) and PO_4–P ($r = –0.478$, $p<0.05$) in the low-tide samples (Table 1). The lower values of DO in low-tide might be due to industrial, domestic wastage and also the influence of salinity, temperature, conductivity, currents, and upwelling tides lead to such changes [38]. The negative correlation of DO with nutrients and BOD might be due to the industrial and domestic effluents released into the region as these are the main sources of oxidizable organic matter [39-40]. The results of DO suggested that the lowest value was beyond the acceptable limits for aquatic life in Kolak, Damanganga, and Par stations. This may be in consequence of the inputs of untreated industrial effluents, domestic sewage, and tidal effect. Zingde et al. [21, 41, 42] have reported the very low values of DO for these estuaries. Several other reports suggested that industrial effluent discharged in Damanganga, Kolak and Par estuaries resulted in the death of fish and aquatic animals and found at the bank of rivers [43-45].

Biochemical Oxygen Demand (BOD) is a lively water quality parameter since it provides an index to evaluate the effect of discharged wastewater on the receiving environment. The increasing level of BOD suggested that the water column is contaminated by organic and nutrients substances inputs in estuaries, especially during the low-tide where the estuarine water intrudes to seawater. The values of BOD varied between 0.42 to 386.42 mg/L in the low-tide and was varied from 1.28 to 178.2 mg/L in the high-tide. The average values of BOD 1.51 ±0.80 mg/L (Varoli), 280.6 ±84.47 mg/L (Damanganga), 187.34 ±100.8 mg/L (Kolak) and 70.98 ±6.48 mg/L (Par) in the low-tide samples. It was 2.12 ±0.60 mg/L(Varoli), 94.12 ±45.55 mg/L(Damanganga), 63.07 ± 55.33 mg/L (Kolak) and 12.06 ±15.58 mg/L (Par) in the high-tide samples (Fig. 2f). Zingde et al. [21, 41] have also found higher values BOD in these estuaries. The results of BOD suggested that the high pollution load in these estuaries has an antagonist effect on the coastal and marine network. High BOD level indicates a decline in DO because the oxygen exists in the water was being consumed by the bacteria leading to the inability of fish and other aquatic organisms to persist in the river. BOD found above permissible limits

[46] in the water samples of Damanganga and Kolak, which showed that these estuaries are under high anthropogenic pressure.

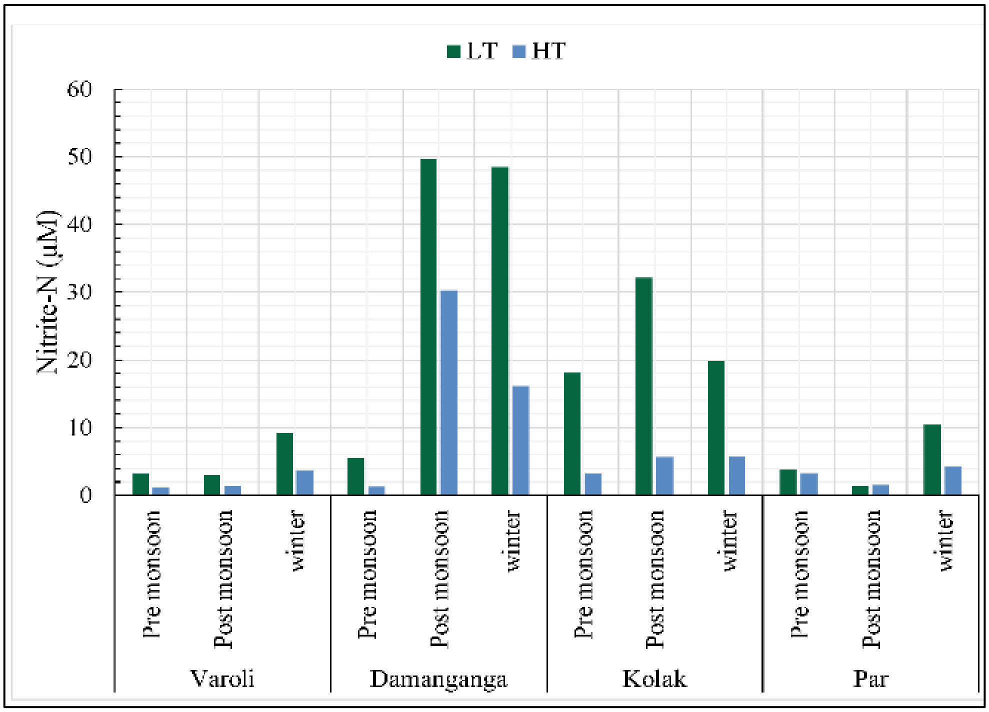

Fig. 3 (a)

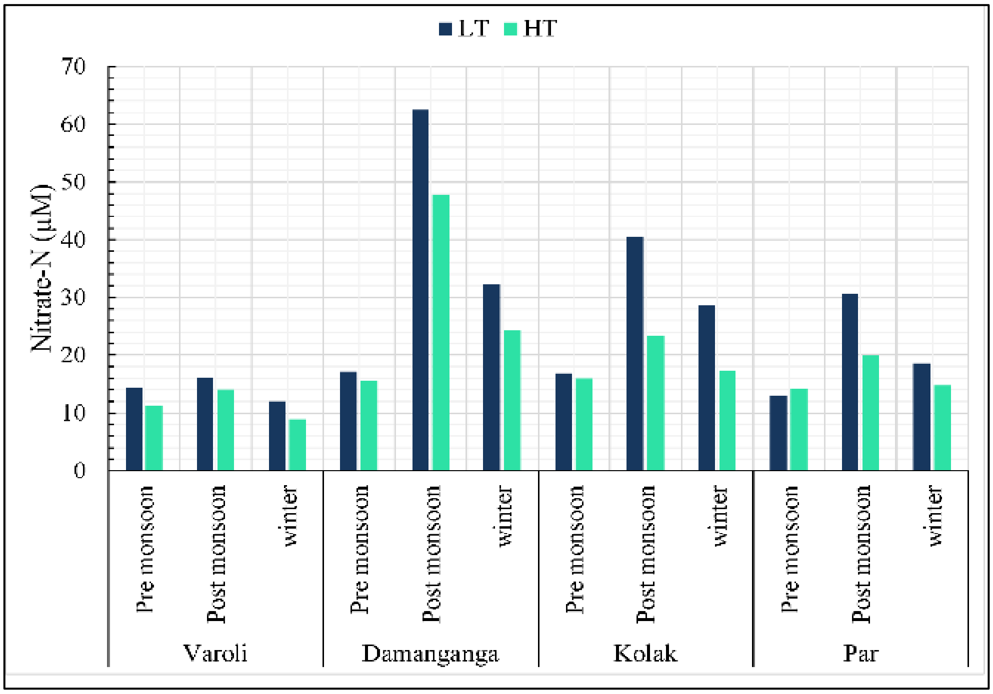

Fig. 3 (b)

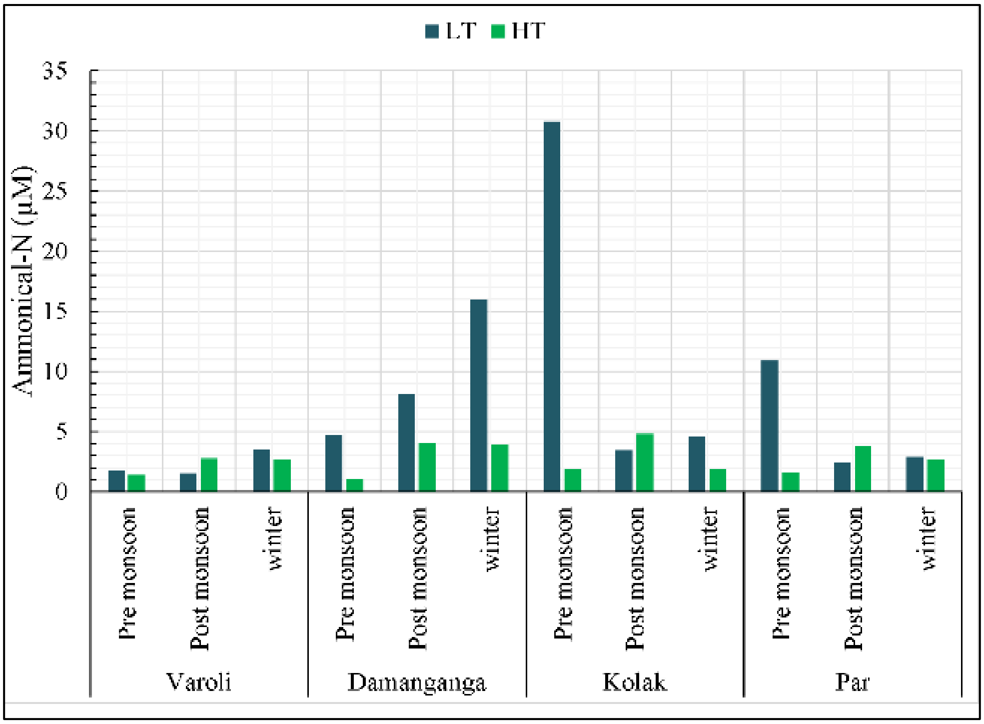

Fig. 3 (c)

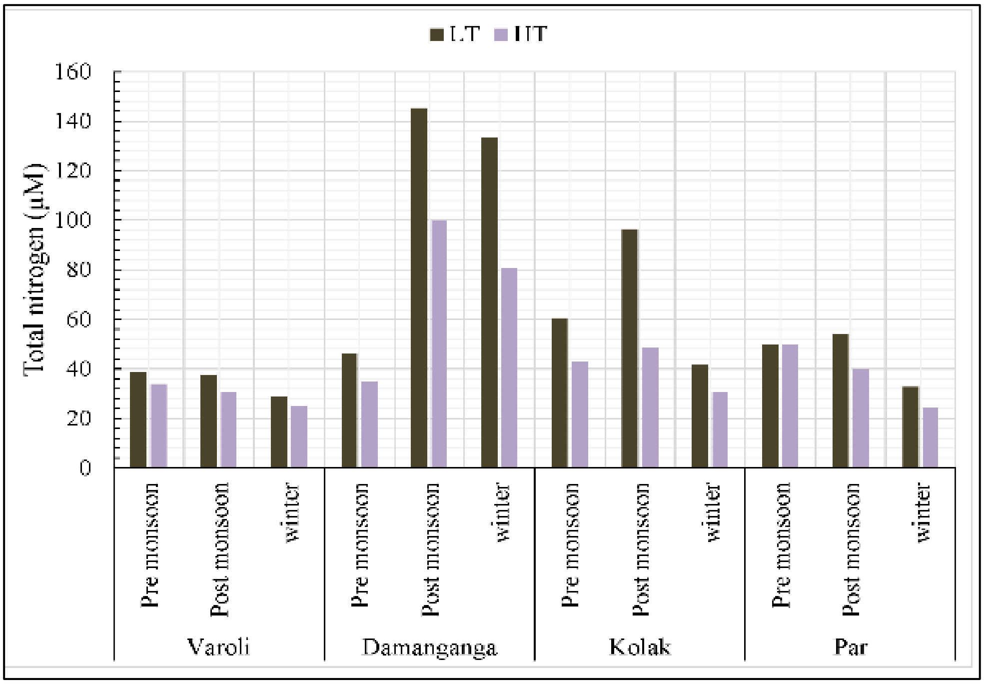

Fig. 3 (d)

Figure 3. Spatial-temporal variation of nutrients; (3a) NO_2-N, (3b) NO_3-N, (3c) NH_4-N and (3d) TN in the surface water during tidal fluctuation at South Gujarat estuaries.

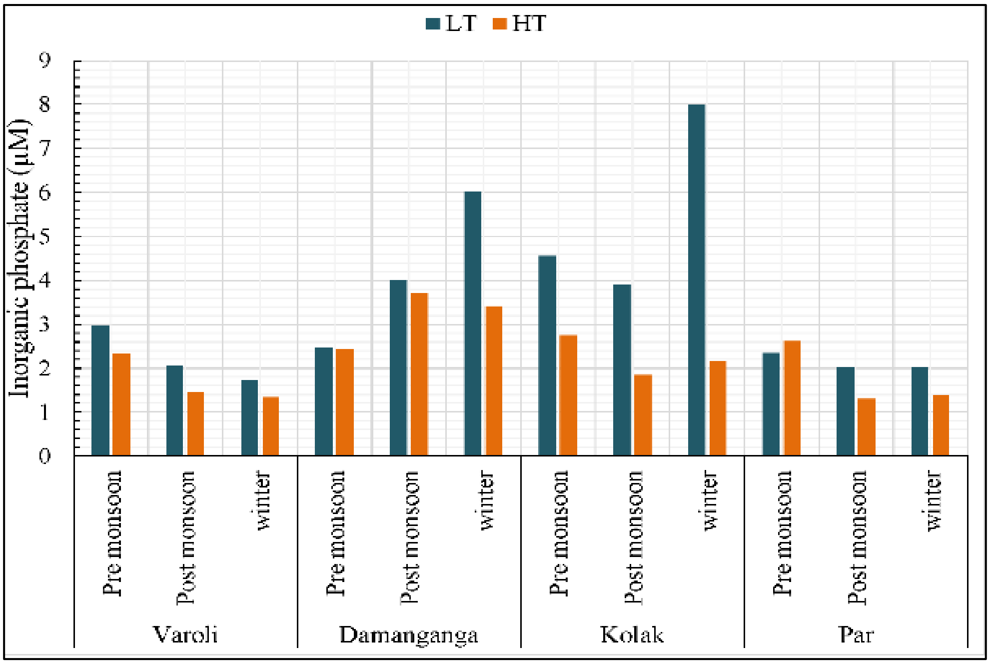

Fig. 4 (a)

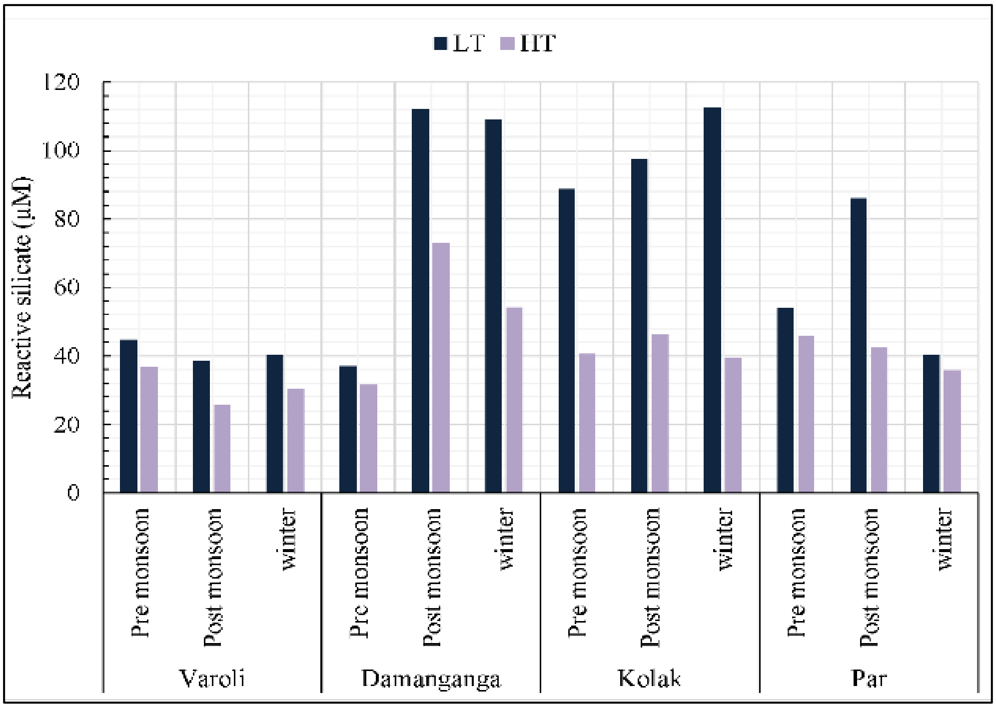

Fig. 4 (b)

Figure 4. Spatial-temporal variation of nutrients (4a) inorganic phosphate and (4b) reactive silicates in the surface water during tidal fluctuation at South Gujarat estuaries.

3. 2. Assessment of nutrients

The nitrogen cycle involves elementary dissolved nitrogen oxides such as (i) NO_3^- and (ii) NO_2^- and reduced forms like (i) NH_4^+ and (ii) NH_3 are playing an important role in sustaining the aquatic life in the marine world. The concentrations of these three major elements are characteristically higher in estuaries than in the open ocean. The domestic and industrial effluents and run-off are the main sources of macro-elements, while the atmosphere and marine waters may also contribute to it in minor amounts.

Nitrate (NO_3–N) is one of the most important markers of pollutions in water and is the highest oxidized form of nitrogen. The most important source of nitrogen is the biological oxidation of organic nitrogenous substances derived from sewage and industrial wastewater or produced indigenously in the water [47]. Zepp [48] observed that variation in nitrate and its reduced inorganic mixtures are predominantly the consequences of biologically activated reactions. The concentration of NO_3–N was oscillating between 8.23 to 70.68 µM in the low-tide and it is varied between 8.92 to 55.35 µM in the high-tide. The average concentration of NO_3–N 14.60 ±2.32 µM (Varoli), 38.28 ±21.68 µM (Damanganga), 28.76 ±12.27 µM (Kolak) and 21.11 ±8.14 µM (Par) in the low-tide samples and 11.86 ±2.35 µM (Varoli), 30.21 ±15.52 µM (Damanganga), 19.17 ±7.0 µM (Kolak) and 16.58 ±3.62 µM (Par) in high-tide samples (Fig. 3b). The highest concentration of NO_3–N was recorded 70.68 µM in the Damanganga for post-monsoon and the minimum was noticed 8.23 µM in the pre-monsoon for Par. The NO_3–N exhibited positive correlation with DO and other nutrients; NO_2–N ($r = 0.784$, $p<0.01$), TN ($r = 0.871$, $p<0.01$), PO_4–P ($r = 0.449$, $p<0.05$), silicate ($r = 0.670$, $p<0.01$) and negatively correlated with pH, salinity and DO in the low tide (Table 1). The low-tide and high-tide results showed similar trends. Quick absorption by phytoplankton and enhancement by surface run-off resulted in a large-scale spatial-temporal variation of nitrate in the coastal region of the Gulf of Khambhat. The results of Edokpayi et al. [49] revealed a similar pattern for nutrient presence in this region.

Nitrite (NO_2–N) is an intermediate in the oxidation process of ammonia to nitrate in the nitrogen cycle. Many industrial, domestic and sewage effluents are rich in ammonia can lead to increase nitrite concentrations in receiving waters. Nitrite is toxic to aquatic life comparatively at low concentrations. The values of NO_2–N were altered 0.75 to 61.71 µM for the low-tide samples and it was between 0.26 to 41.69 µM for the high tide samples. The average concentration of NO_2–N was 5.13 ±3.53 µM (Varoli), 34.57 ±22.89 µM (Damanganga), 23.38 ±14.49 µM (Kolak) and 5.17 ±5.12 µM (Par) for the low-tide samples and 2.07 ±1.90 µM (Varoli), 15.88 ± 14.9 µM (Damanganga), 4.85 ±2.15 µM (Kolak) and 3.02 ±1.59 µM (Par) for the high-tide samples (Fig. 3a). The highest concentration of NO_2–N was 61.71 µM in winter and the lowest was 1.13 µM in the Damanganga estuary in the low-tide samples for pre-monsoon. The negative correlation with salinity ($r = –0.815$, $p<0.01$) suggested that during the low-tide the concentration of NO_2–N increased. This may be attributed to the industrial effluent and domestic wastage inputs in these estuaries.

Ammonia is present in terrestrial and marine environments where the plants and animals were expelled ammonia. It is produced by the decay of organisms and by the commotion of living micro-organisms [50]. Ammonium ion (NH_4^+) represented 80% of dissolved inorganic nitrogen (DIN) and its highest values are always associated with freshwater invasion [33]. Sankaranarayanan and Qasim [51] suggested that the three-dimensional and time-based variation in ammonia concentration might also be due to its oxidation to other forms or reduction of nitrates to lower forms in coastal waters.

The concentration of ammonical–nitrogen (NH_4–N) was varied from 1.05 to 30.78 µM in the low-tide samples and altered between 1.08 to 5.22 µM for the high-tide samples. The average concentration of NH_4–N was 2.38 ±1.01 µM (Varoli), 10.56 ±5.63 µM (Damanganga), (10.78 ±9.36 µM (Kolak) and 4.303 ±3.32 µM (Par) for low-tide and 2.47 ±0.57 µM (Varoli), 3.35 ±1.49 µM (Damanganga), 3.01 ±1.46 µM (Kolak) and 2.90 ±0.95 µM (Par) for high-tide respectively (Fig. 3c). The maximum value of NH_4–N was noticed 30.78 µM in the Par during low-tide in the pre-monsoon and minimum concentration was obtained 1.05 µM in the Varoli during low-tide for post-monsoon. The NH_4–N positively correlated to turbidity and was negatively correlated with salinity, conductivity and DO for the low-tide samples and was negatively correlated with salinity, turbidity, and conductivity for the high-tide samples.

Total nitrogen (TN) is the measure of all forms of nitrogen (organic and inorganic). The importance of nitrogen in the aquatic environs is patchy according to the relative amounts of the forms of nitrogen present, be it ammonia, nitrite, nitrate, or organic nitrogen. The concentration of TN was ranging from 28.66 to 152.36 µM in the low-tide and was varied from 24.22 to 110.98 µM in the high-tide samples. The average concentration of TN was 36.15 ±4.02 µM (Varoli), 103.17 ±47.59 µM (Damanganga), 71.03 ±28.18 µM (Kolak) and 48.02 ±10.52 µM (Par) for the low-tide and average concentration was 30.77 ±3.77 µM (Varoli), 69.92 ±30.45 µM (Damanganga), 42.62 ±6.96 µM (Kolak) and 40.75 ±11.21 µM (Par) for the high-tide (Fig. 3d). The concentration of TN was highest in the Damanganga (152.36 µM) and lowest (24.22 µM) in the Par in the winter season respectively. There is all-encompassing evidence that an increase in nitrogen loads are linked to eutrophication in the estuaries [52] and displayed an impact on aquatic life and microorganism.

Phosphate in coastal waters depends upon its concentration in the freshwater that mixed with the seawater [53]. Inorganic phosphate is the most readily accessible form of uptake during photosynthesis in the aquatic ecosystem and enrichment of phosphate causes eutrophication, which leads to aggregation with algal blooms, resulting in the depletion of DO level in estuaries. The concentration of inorganic phosphate (PO_4–P) was varied between 0.788 to 10.22 µM and 0.45 to 5.63 µM in the low-tide and high-tide samples respectively. The average concentration of PO_4–P was 2.26 ± 0.98 µM (Varoli), 4.16 ±2.28 µM (Damanganga), 5.48 ±2.82 µM (Kolak) and 2.13 ±0.93 µM (Par) was noticed during the low-tide and average values were 1.71 ±0.80 µM (Varoli), 3.18 ±1.34 µM (Damanganga), 2.25 ±0.50 µM (Kolak) and 1.77 ±0.77 µM (Par) (Fig. 4a) in the high-tide. Industrial effluents, as well as domestic wastage released around Damanganga, Silvasa, Vapi GIDC, Valsad GIDC, and CETP at Vapi and other creaks located around industries, maybe the major contributors of phosphate into south Gujarat estuarine environment. Liu et al. [54] have reported that seawater serves as the main source of phosphate in the estuarine and coastal waters except for those receives freshwater contaminated with industrial and domestic waste containing detergents as well as waste from an agro field rich with phosphate-phosphorous fertilizers and pesticides. The noticeable seasonal deviation in the phosphate concentration might be due to various processes like adsorption and desorption of phosphate and buffering action of sediments under varying conservational conditions [55].

The silicate is one of the important nutrients that regulate the phytoplankton distribution in the estuaries and also useful for other living organisms in the estuarine area. The concentration of reactive silicate (SiO_4–Si) ranging from 21.56 to 131.18 µM in the low-tide and was altered between 23.75 to 102.72 µM in the high-tide samples respectively. The average concentration of silicate was in the Varoli (40.50 ±7.76 µM), Damanganga (95.92 ±32.80 µM), Kolak (101.71 ±9.96 µM) and Par (61.37 ±28.99 µM) in the low tide and the average values of reactive silicate were found in the Varoli (29.91 ±4.47 µM), Damanganga (57.15 ±29.02 µM), Kolak (42.51 ±6.80 µM) and Par (40.45 ±7.40 µM) during the high-tide (Fig. 4b). The highest concentration of silicate was found in the samples of Damanganga (131.18 µM) in the post-monsoon. The variation of silicate in coastal water is influenced by the physical mixing of seawater with freshwater, adsorption into sedimentary particles, chemical interaction with clay minerals, co-precipitation with humic components and biological removal by phytoplankton, especially by diatoms and silicoflagellates [56]. Silicate showed a negative correlation with salinity and in the low-tide salinity decreased and the concentration of silicate exceedingly increased. The main source of silicates in these coastal water regions is the entry of silicates through land drainage, which is richened in the weathered silicate material [57].

3. 3. Principal components analysis (PCA)

Principal components analysis (PCA) has been used on a correlation matrix of rearranged data to explain the structure of the underlying dataset and to identify the unobservable, latent pollution sources. PCA of water quality parameters and nutrient measurements derived from the low-tide and the high-tide samples and data suggested that there were three composite variables (hereafter PC1, PC2, and PC3). Twelve parameters were used in PCA such as pH, salinity, conductivity, turbidity, DO, BOD, NO_2-N, NO_3-N, NH_4-N, TN, phosphate and reactive silicates. The PCA suggested the percentage of alterability of PC1 (57.41 %,), PC2 (17.58%) and PC3 (9.58%) for low-tide samples and is depicted in Fig.5 and summarized in Table 3. PC1 exhibited a positive loading of BOD, NO_2-N, NO_3-N, TN, phosphate, reactive silicates and had a negative correlation with pH, salinity, conductivity and DO.

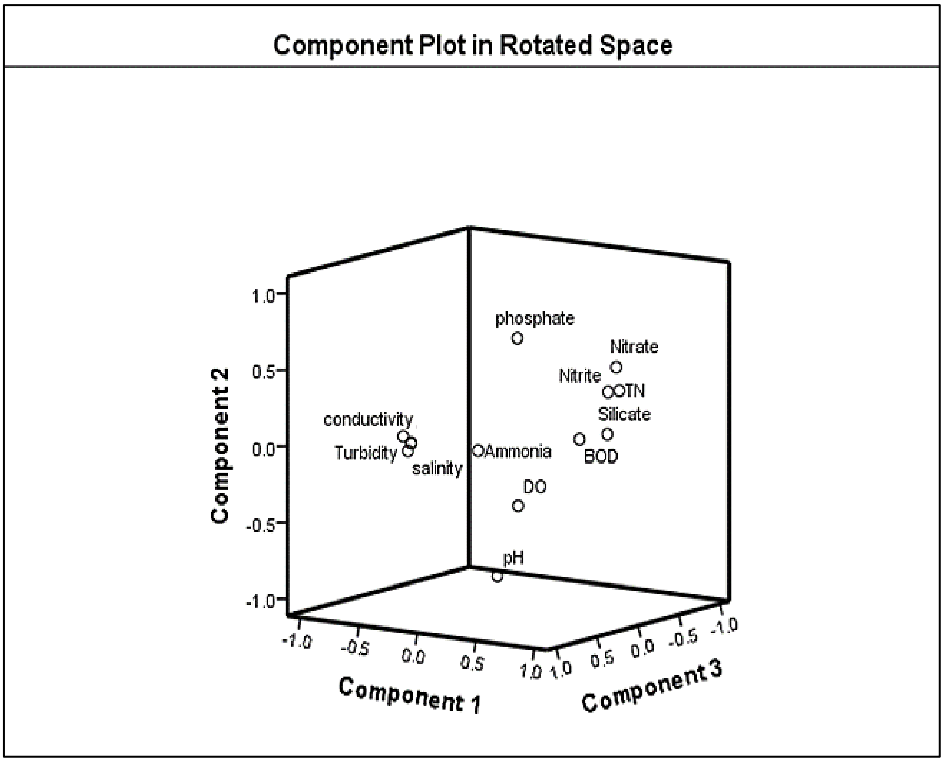

Figure 5. PCA diagram for low tide behavior of water quality parameters

Table 3. Loading of water quality parameters on the principal component at low tide

Variable	**Low tide**		
	Principal component		
	1	**2**	**3**
pH	-0.516	-0.299	0.721
Salinity	-0.958	0.104	-0.192
Conductivity	-0.943	0.085	-0.245
Turbidity	-0.028	0.946	0.173
DO	-0.612	-0.597	0.146
BOD	0.723	-0.037	0.219
NO_2-N	0.896	-0.167	-0.082
NO_3-N	0.812	-0.323	-0.311
NH_4-N	0.488	0.702	0.380
TN	0.875	-0.289	-0.123
Phosphate	0.628	0.422	-0.411
Reactive silicate	0.859	-0.177	0.196
Eigenvalue	7.463	2.286	1.246
Variance (%)	57.411	17.585	9.585
Cumulative	57.411	74.996	84.581

Extraction Method: Principal Component Analysis
Component Matrix^{a} a. 3 components extracted

The data of PC1 flourished the loading pattern of dissolved nutrients and BOD. A positive correlation of BOD with nutrients is attributed to inputs of industrial and sewage wastage in estuarine waters. PC2 revealed a positive loading of turbidity, NH_4-N and had a negative association with pH and DO, whereas PC3 showed a positive loading for pH, which suggests that contribution of pH variability in water depends only on PC3. The percentage of the unpredictability of PC1 (53.50 %,), PC2 (19.92%) and PC3 (9.62%) for the high-tide samples and is depicted in Fig. 6 and a set of data presented in the Table 4.

PC1 showed a high positive loading of BOD, NO_2-N, NO_3-N, NH_4-N, TN, reactive silicates and had a negative relationship with salinity, conductivity, turbidity and DO. PC2 flaunted a positive loading of phosphate, salinity, conductivity and had a negative correlation with NH_4-N, pH and DO, whereas PC3 had a positive loading for pH, DO and BOD. The negative relationship between nutrients and DO was observed in the PCA may be due to the consumption of large amounts of oxygen by organic matters [58-59]. The comparison of PCA during the low-tide and high-tide suggested that the water quality parameters and loading trend had quite a similar pattern but NH_4-N, phosphate and turbidity loading pattern was found different in both situations.

Table 4. Loading of water quality parameters on the principal component at high tide

Variable	**High tide**		
	Principal component		
	1	**2**	**3**
pH	-0.372	-0.418	0.762
Salinity	-0.926	0.361	-0.023
Conductivity	-0.918	0.380	-0.041
Turbidity	-0.653	0.187	0.065
DO	-0.595	-0.246	0.343
BOD	0.671	0.073	0.469
NO_2-N	0.763	0.457	0.332
NO_3-N	0.753	0.536	-0.140
NH_4-N	0.640	-0.549	-0.393
TN	0.839	0.413	0.076
phosphate	0.235	0.942	0.110
Reactive silicate	0.856	-0.193	0.148
Eigenvalue	6.956	2.59	1.251
Variance (%)	53.504	19.923	9.625
Cumulative	53.504	73.427	83.052

Extraction Method: Principal Component Analysis
Component Matrix^a a. 3 components extracted.

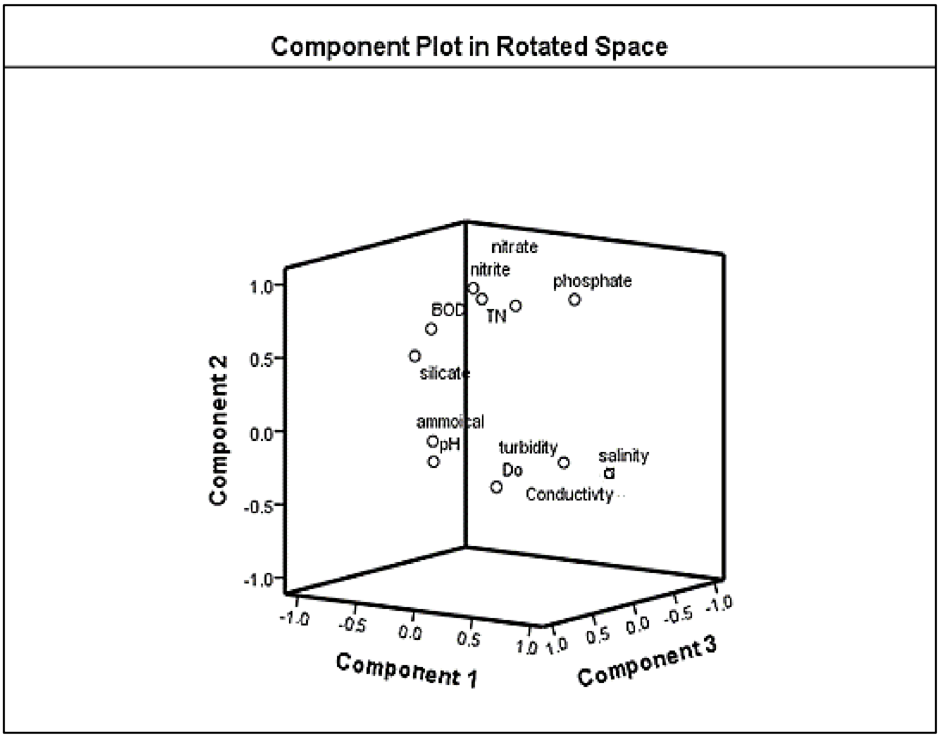

Figure 6. PCA diagram for high tide behavior of water quality parameters

4. CONCLUSIONS

The study provides seasonal, tidal and spatial-temporal of hydrological regime of the estuarine bio-network of the South Gujarat region. During the monsoon season, the salinity of estuarine water reduced due to the high incursion of the freshwater into the seawater. The major nutrients showed significant seasonal transformations in the concentration levels and in some cases, tidal variations were also witnessed. Similarly, DO, BOD and other water quality indicators showed dissimilarities in the different seasons. The present investigation also showed that the physico-chemical properties of the coastal water of the South Gujarat estuarine region were emphatically affected by freshwater inflow and industrial waste influx, especially during the low-tide. PCA and Pearson's correlation coefficient showed that very little freshwater input during non-monsoon seasons and high nutrient input from sewage and industrial discharges and other point sources of pollution have caused localized problems of the water quality of the estuaries of South Gujarat. The study area was under heavy pressure of industrial waste and high anthropogenic activities.

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