Physico-chemical characteristics of the coastal water off Devi estuary, Orissa and evaluation of its seasonal changes using chemometric techniques

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Devi estuary is one of the major tributaries of the Mahanadi riverine system in Orissa. Modernization and industrialization in its neighbourhood in the north in the recent past have greatly influenced many tributaries of the Mahanadi and the adjacent coastal environments. To trace the influence of this modernization activity further down south off Devi estuary and to understand the quality of the Devi estuarine water reaching the coastal region, investigations on physico-chemical parameters (temperature, pH, salinity, dissolved oxygen), including dissolved nutrients (PO_4-P, NO_3-N, NO_2-N, SiO_4-Si) were carried out in the water off the mouth of the Devi estuary, during different months of the summer and winter seasons in 2006–07. The multivariate statistics and principal component analysis applied to the datasets, indicated three factors each during the summer and winter seasons influencing the water to the extent of 77 and 80% respectively. Principal axis factoring and alpha factoring have been used to observe the mode of association of parameters and their interrelationships, for evaluating water quality during the summer and winter seasons. The results indicated the addition of phosphates and silicates to the coastal water by the Devi estuary from natural sources during both the seasons. The anthropogenic nitrogenous species, as a fallout from modernization activities in the north, are more clearly observed off the mouth of the Devi estuary during the winter season. The study indicated that the Devi estuary adds sufficiently well-oxygenated, nutrient-rich water to the coastal region.

Keywords: Coastal environment, multivariate statistics, physico-chemical parameters, principal component analysis, seasonality.

RIVERS are the main inland water resources for domestic, industrial and irrigation purposes and often carry large municipal sewage, industrial wastewater discharges and seasonal run-off from agricultural land to the coastal region. It is for this reason that the river water is mostly enriched in nutrients compared to other environments[1]. The spatial heterogeneity within the river, however, is due to existing local environmental conditions such as light, temperature, water discharge and flow velocity that change with time, and differences in the local channel form[2]. Contrary to this, the coastal environments are highly economical, important and are significantly involved in the transport of terrestrial organic matter and associated nutrient elements to the sea for their biogeochemical cycling. The balance in the concentrations of bio-geogenic elements in coastal water reflects the healthy status of water, while their excess supply as observed in the continental shelf and upwelling areas has been found to trigger high primary productivity[3,4]. The complex dynamism in physico-chemical characteristics of coastal waters is related to riverine flow, upwelling, atmospheric deposition, vertical mixing and other anthropogenic sources.

The coastal Bay of Bengal is a unique marine environment in the tropical belt with marked continental influence due to the drainage by a large number of rivers. One such riverine system is the Mahanadi river in Orissa, which is the third largest river in India. The three major urban settlements such as Cuttack, Sambalpur and Paradeep along the banks of this river have resulted in a large amount of untreated domestic waste and effluents from fertilizer, paper, textile distilleries and many other industries in Orissa[5]. The Mahanadi river divides into many branches and one of its main branches is the Devi river, which meets the Bay of Bengal at Nuagarh. Due to various anthropogenic influences in the Mahanadi river basin, large amounts of contaminants arising from nutrients and other parameters have been observed in many of its tributaries and the adjacent coastal region[1]. Apart from this, the naturally occurring cyclones along the Orissa coast, which give rise to severe floods, also affect the water quality and productivity of the waters off the Orissa coast. There is hardly any information available on the water quality characteristics of the Devi river compared to other estuaries along the east coast. It is important to know the additions to the coastal water from the Devi

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estuary because it is well-known place for the congregation of Olive ridley turtles during their arribada. In view of this, physico-chemical studies were carried out at selected locations in the coastal region off the mouth of the Devi estuary (Figure 1) in the summer and winter seasons of 2006–07 to assess the water quality of the region and to understand its input to the coastal water. The present study also aims to find out the seasonal variations in physico-chemical parameters of the coastal water off the mouth of the Devi estuary and the anthropogenic influence.

Study area

The Devi estuary (86°23′36.5″E, 19°57′43.2″N) belongs to the Mahanadi river basin in Orissa, along the northeast Bay of Bengal. The Mahanadi river is a biggest river in Orissa, which originates in the Baster Hills of Madhya Pradesh, flows over different geological formations of the Eastern Ghats and joins the Bay of Bengal, after dividing into different branches in its deltaic region[6]. The main branches of the Mahanadi river meet the Bay of Bengal at Paradeep and Nuagarh (Devi estuary). The basin extends[7] over an approximate area of 141,600 sq. km, with a total length of 851 km and a peak discharge of 44,740 $m^3 s^{-1}$. The inland geographical area of the basin experiences extremely continental climate. The total amount of renewable water resources in the basin is to the extent of 66.9 km^3. The annual average rainfall is 1572 mm, of which 70% is during the southwest monsoon (June–October), with a maximum during July–September[8]. The mean annual temperature is about 26.2 (± 0.4)°C, with a winter minimum of 20.9 (± 0.7)°C (December–January) and a summer maximum of about 30.1 (± 0.7)°C (March–April)[9]. In all, the three principal seasons, i.e. summer, monsoon and winter are experienced in this basin.

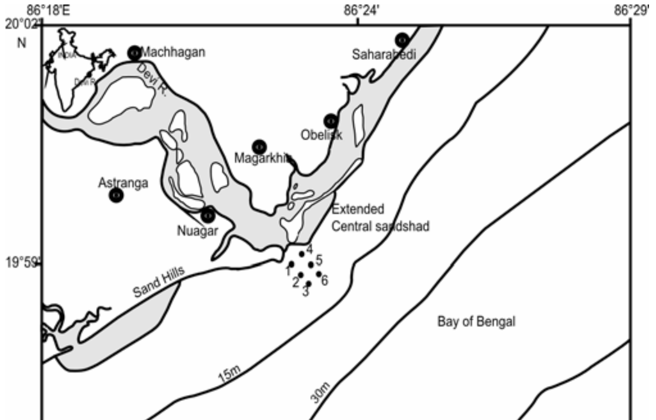

Figure 1. Map of the study area showing station location points.

The basin geology is characterized by Precambrians of the Eastern Ghats. The lithology consists of granite covering 34% of the basin area, khondalite (7%), charnockite (15%), limestone, shale of Lower Gondwana (17%), sandstone, shale of Upper Gondwana (22%) and coastal alluvium (5%). A part of the richest mineral belt of the sub-continent consisting of Fe-ore, coal, limestone, dolomite, bauxite, Pb and Cu deposits falls within this basin[10]. The Mahanadi basin is one of the five sedimentary basins occurring along the east coast of India. The morphological structure of this environment is highly dynamic, where processes of erosion, accretion and deposition are active. Along its course, the Mahanadi river receives effluents from different industrial and urban centres such as Sambalpur, Cuttack, Choudhar, Jagatpur and Paradeep[5]. It also receives a large amount of agricultural run-off along its course. The human influences are more pronounced at Sambalpur, Cuttack and Paradeep due to the presence of a large number of industrial and sewage discharges. The different trend of lineament in the northern and southern parts of the Mahanadi river causes growth of spit near the Devi river mouth and forms an estuarine-type of delta, where most of the depositional activities are within the Devi river[11].

Material and methods

A total of 60 water samples from six selected stations along two transects extending from the mouth of the river towards the offshore region, as shown in Figure 1, were drawn from the surface and bottom layers during the summer and winter seasons of 2006–07, using Niskin water sampler. The physico-chemical parameters such as pH, dissolved oxygen (DO), phosphate (PO_4-P), nitrite (NO_2-N), nitrate (NO_3-N) and silicate (SiO_4-Si) were measured according to the standard procedures[12,13]. The data quality was ensured through careful standardization, procedural blank measurements, spike and duplicate samples. Measurements of *in situ* temperature (°C) and salinity (psu) were made using probes, while DO was measured using Winkler's method[14].

Multivariate statistics

Principal component analysis (PCA) is one of the best statistical techniques for extracting linear relationships among a set of variables[15]. Principal components are the linear combinations of original variables and are the eigenvectors[16]. The Varimax rotation distributes the PC loadings such that their dispersion is maximized by minimizing the number of large and small coefficients[17]. The normalized, promax-rotated principal axis factoring (PFA) eliminates the variance due to unique factors, that are uncorrelated with one another and with the common factor, and is thus excluded from our factor analysis. The reproduced and residual correlation matrix indicates that the factors indeed do capture the relationships between variables by calculating correlations between them and the correlations between factors and variables. The reliability (alpha) or alpha factor analysis (AFA) attempts to create factors which are linear combinations of the variables, to estimate the 'latent variables' or constructs which the instrument measures[18]. In this study, the exploratory data analysis techniques have been applied separately to datasets on physico-chemical parameters collected during the summer and winter seasons and the results obtained on the basis of various natural and anthropogenic conditions are highlighted.

Results and discussion

The datasets have been collected separately in the summer and winter months and the scree plot for both the seasons shows the amplitude of different eigenvectors against their principal components (PCs; Figure 2). The ranges of variation, mean and standard deviation and the variation of parameters with their standard error are shown by box plots (Figure 3 *a* and *b*). A data matrix of 90 observations was processed separately for both the seasons through multivariate statistical analyses (SPSS 16.0). The cornbach's alpha (0.892) and Kaiser–Meyer–Olkin (KMO) sample adequacy to the order of 0.885 show the appropriate application of factor analysis in the present data matrix. The varimax-rotated and normalized factors were extracted through various methods such as PCA and PAF. Adjusted eigenvalues greater than one were further cleaned up using this technique and in varifactors; the original variable participated more clearly. Liu *et al.*[19] have classified the factor loading as strong (>0.75), moderate (0.75–0.50) and weak (0.50–0.40). Residual correlation among the parameters has been determined from descriptive and reproduced correlation matrix that results in low percentage (10) of the non-reductant residuals in the dataset.

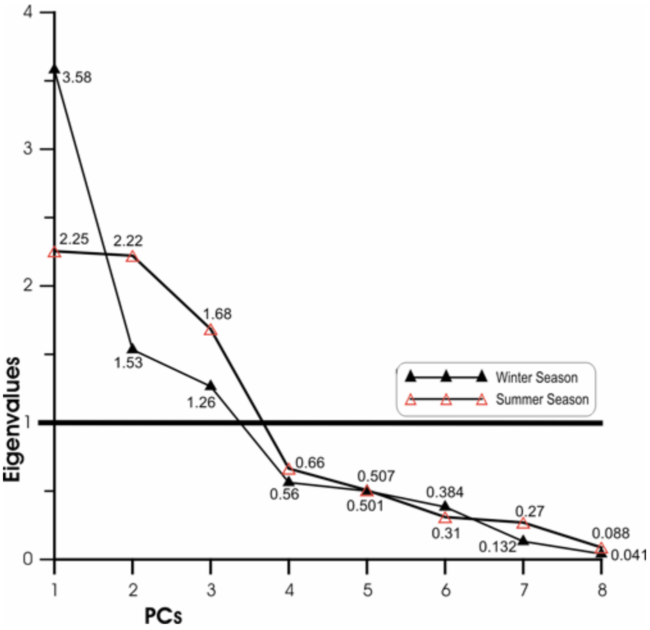

Figure 2. Scree plot between different principal components (PCs) and their eigenvectors.

Winter season

The three factors or PCs explain 79.74% of the total variance during winter season (Table 1). PC1 accounts for 38.26% of the total variance, which is due to strong positive load of phosphate phosphorus (0.941), silicates (0.848) and temperature (0.806) and a strong negative load of salinity (–0.809), with significant positive correlations of temperature with phosphate phosphorus ($r = 0.79$) and silicates ($r = 0.67$) and their negative correlations with salinity (Table 2). Besides, the significant positive correlation between phosphate and silicates (Table 2) indicates a common source for both, and suggests that the phosphate and silicate content increases in low-salinity water, which is a riverine-source water com-

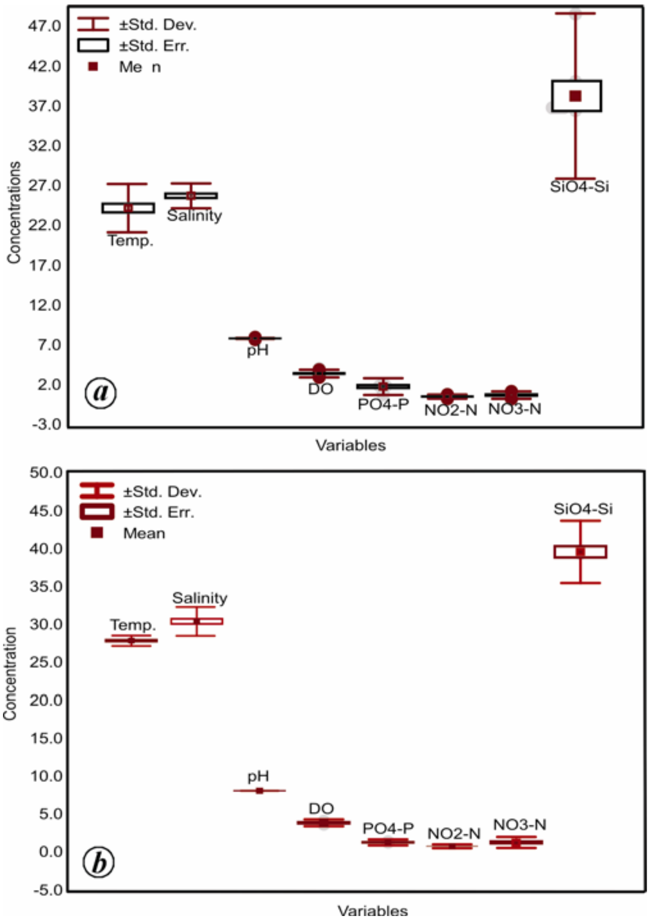

Figure 3. Box plot showing variation of physico-chemical parameters during (***a***) winter and (***b***) summer seasons.

Table 1. Rotated component matrix (RCM) with varifactors (principal components, PCs) and extracted communalities in two seasons

Winter season					Summer season				
RCM	PC1	PC2	PC3	Communality	RCM	PC1	PC2	PC3	Communality
PO_4	0.941	0.216	0.060	0.903	PO_4	0.821	–0.038	–0.307	0.663
SiO_2	0.848	0.172	0.023	0.682	SiO_2	0.812	0.215	0.367	0.908
Salinity	–0.809	0.042	0.160	0.796	Salinity	0.774	0.046	0.520	0.126
Temperature	0.806	0.160	0.477	0.881	Temperature	0.421	–0.809	0.002	0.492
pH	–0.008	0.892	–0.001	0.936	pH	0.127	0.776	0.356	0.212
NO_2	0.180	0.826	–0.096	0.724	NO_2	–0.269	–0.760	0.269	0.233
NO_3	0.340	0.598	0.484	0.707	NO_3	0.230	0.580	0.518	0.784
DO	–0.058	–0.085	0.933	0.749	DO	0.034	0.004	0.847	0.844
Eigenvalue	3.061	1.947	1.371		Eigenvalue	2.254	2.221	1.685	
% Variance	38.262	24.34	17.13		% Variance	28.173	27.76	21.06	
Cumulative%	38.262	62.6	79.74		Cumulative%	28.173	55.93	76.99	
KMO adequacy = 0.776					KMO adequacy = 0.784				

Temperature in °C; salinity in psu; DO in ml l^{-1}; phosphate, nitrite, nitrate and silicates in μmol/l.

Table 2. Correlation matrix between physico-chemical parameters in different seasons

	Temperature	Salinity	pH	DO	PO_4-P	NO_2-N	NO_3-N	SiO_4-Si
Winter								
Temperature	1.000							
Salinity	–0.580	1.000						
pH	0.162	–0.005	1.000					
DO	0.347	0.132	–0.053	1.000				
PO_4-P	0.786	–0.648	0.167	–0.035	1.000			
NO_2-N	0.215	–0.158	0.577	–0.067	0.318	1.000		
NO_3-N	0.583	–0.179	0.447	0.228	0.502	0.394	1.000	
SiO_4-Si	0.668	–0.462	0.166	0.003	0.886	0.298	0.281	1.000
Summer								
Temperature	1.000							
Salinity	0.282	1.000						
pH	0.261	0.341	1.000					
DO	0.600	0.537	0.260	1.000				
PO_4-P	0.030	0.370	–0.123	0.006	1.000			
NO_2-N	–0.396	–0.105	0.075	–0.274	–0.152	1.000		
NO_3-N	0.366	0.799	0.377	0.361	0.486	–0.312	1.000	
SiO_4-Si	–0.514	0.303	–0.039	–0.306	0.288	0.419	0.103	1.000

Temperature in °C; salinity in psu; DO in ml l^{-1}; phosphate, nitrite, nitrate and silicate in μmol/l.

ing from the hinterlands. Thus, the riverine water adds phosphate and silicates to the coastal region (Figure 4 *e* and *h*) and this factor therefore suggests a riverine source.

PC2 explains 62.6% of the total variance with strong positive loading of pH (0.892) and NO_2-N (0.826) and a moderate positive loading of NO_3-N (0.598), with significant positive correlations (Table 2). The strong positive correlation between pH and NO_2-N ($r = 0.58$) suggests that the increasing pH of water is associated with increasing nitrogenous species. The pH of water increases away from the mouth of the river and is concomitant with increases in nitrite, which is seen as a patch in the north-south direction (Figure 4 *c* and *f*). Comparatively, the less significant correlation between pH and NO_3-N ($r = 0.45$) indicates the addition of NO_3-N from the northward direction (Figure 4 *c* and *g*). The possible reason for this are the anthropogenic sources, i.e. waste discharges in the coastal water, mostly from fertilizer industries present in the north of the Devi estuary in Paradeep[20]. The wastes discharged into the tributary of the Mahanadi river at Paradeep enters the coastal region off Paradeep and travels southwards due to the south-flowing current during winter and its effect is seen in the coastal water off Devi estuary (Figure 4 *f* and *g*). This factor therefore indicates an industrial source.

PC3 is strongly loaded positively by DO (0.933), weakly loaded positively by NO_3-N (0.484) and temperature (0.477), with no significant correlations between them. The less saline riverine water from the Devi estuary is enriched with DO, as can be seen from Figure 4 *d*, which shows a tongue of high concentration of DO of 4.14 ml/l, extending from the Devi estuary into the coastal water, where the DO decreases to as low as 4.06 ml/l in the mixing zone. However, the reason for observing low DO in the mixing zone is the polluted, low-salinity water, which comes from the tributary of the Mahanadi at Paradeep towards north of the Devi estuary. When this water mixes with the Devi estuary water, it decreases the DO content in the mixing zone. Studies by Sundaray *et al.*[20] in Mahanadi river–estuarine system have indicated that large amounts of acidic industrial effluents are discharged into the estuary by the fertilizer industrial units located in Paradeep. Besides, the Atharbanki creek near Paradeep receives high organic load from the sewage of Paradeep Port Trust Township and the Fertilizer Industries. This decreases the DO of water in the Paradeep area and the mixing of this water with the Devi estuary water therefore reduces the DO. However, beyond the mixing zone, the water is again well oxygenated and this well-oxygenated water is added to the coastal region. This is evident from Figure 4 *d*, which suggests DO to fall as low as 3.98 ml/l in the mixing zone and then increase further from 4.02 to 4.1 ml/l beyond, indicating oxygenation of the water column.

The interrelationships among the varifactors were found from the correlation between them through component transformation matrix and biplot between PC1 and PC2, wherein the scores of samples drawn and the loadings of variables have been plotted (Figure 5 *a*). The results showed the salinity and pH to be present in the first quadrant, indicating an alkaline condition arising due to coastal sea-water influence. Other parameters such as NO_3-N, NO_2-N, PO_4-P, SiO_4-Si, DO and temperature present in the second quadrant show close association between these parameters, which can be interpreted as the utilization of inorganic nutrients supporting the photosynthetic process that helps regenerate DO.

Summer season

During summer months, three factors account for 76.99% of the total variance (Table 1). PC1 explains 28.17% of the total variance, associated with strong positive loading of PO_4-P (0.821), SiO_4-Si (0.812) and salinity (0.774) with a weak positive loading of temperature (0.421), with no significant correlations between them. However, the strong positive loadings of phosphate and silicates indicate their dominance in water near the river mouth, which are contributed by the river to the coastal water (Figure 6 *e* and *h*) due to weathering and transport, as observed for the winter season. This indicates a riverine source.

PC2 accounts for 55.93% of the total variance and is associated with strong positive loading of pH (0.776), moderate loading of NO_3-N (0.580), strong negative loadings of temperature (–0.809) and NO_2-N (–0.760), with no significant correlations between them. However, the negative correlation of nitrate with nitrite is not significant,

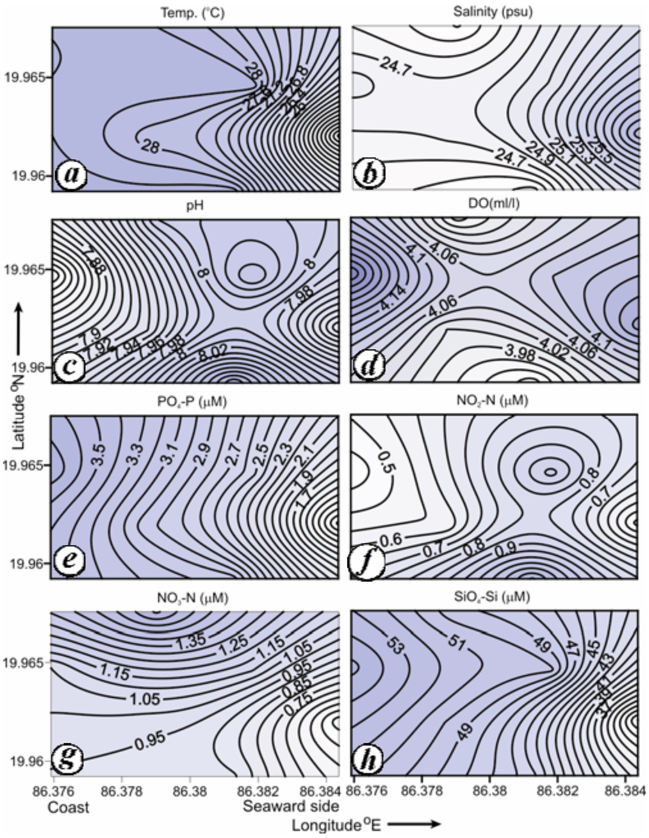

Figure 4. Contours showing variation in physico-chemical parameters at stations 1–6 during winter season.

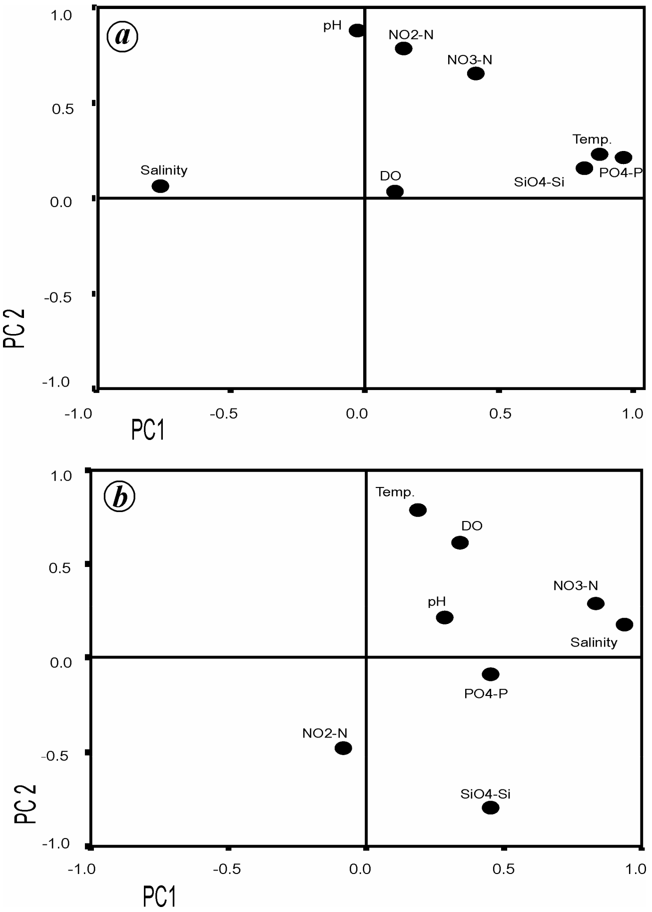

Figure 5. Biplot showing loadings of physico-chemical variables during (***a***) winter and (***b***) summer seasons.

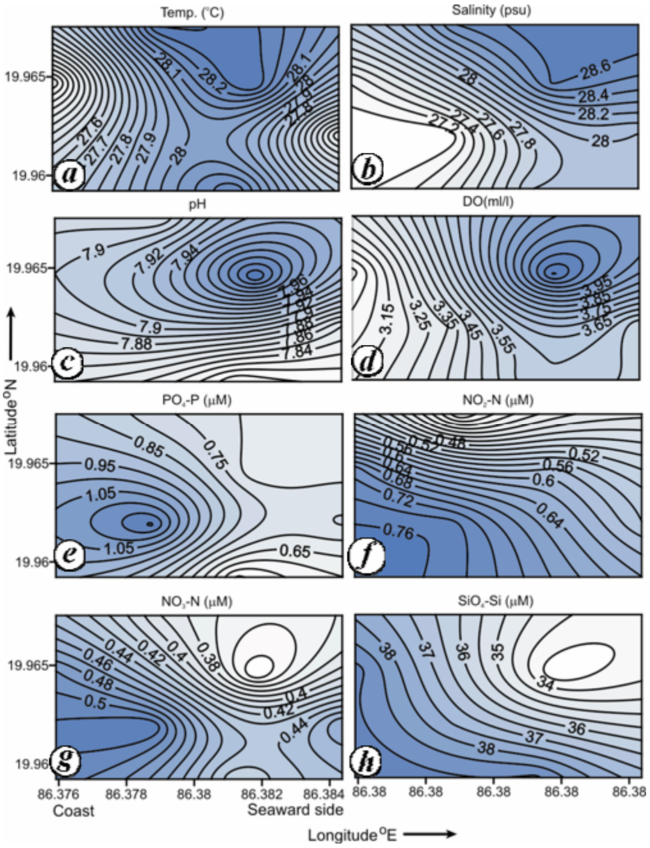

Figure 6. Contours showing variation in physico-chemical parameters at stations 1–6 during summer season.

while the positive correlation of pH with both is also not significant. The contours show lower concentrations of NO_3-N (0.36 to >0.5 μmol/l) and NO_2-N (0.48 to >0.72 μmol/l) during summer compared to those during winter, which shows higher values of NO_3-N (0.75 to >1.35 μmol/l) and NO_2-N (0.6 to >0.9 μmol/l). The observed concentrations of nitrogenous species during summer are low, and can be considered to be those normally observed in unpolluted environments. So, the Devi estuary adds low concentrations of both the nitrogenous species to the coastal water (Figure 6 *f* and *g*).

PC3 accounts for 76.99% of the total variance and indicates strong positive loading of DO (0.847), moderate positive loadings of NO_3-N (0.518) and salinity (0.52), with significant correlations of salinity with DO and NO_3-N. This indicates that despite the increasing salinity by evaporation in summer, the near-shore coastal water off the Devi estuary remains well oxygenated, with minor additions of nitrogenous species from the Devi estuarine water.

The biplot observed between PC1 and PC2 shows salinity, pH, NO_3-N, DO and temperature to be present in the second quadrant, suggesting strong association between these variables (Figure 5 *b*). Other parameters such as PO_4-P and SiO_4-Si are present in the third quadrant. There is a close association between these parameters, which can be interpreted as a similarity between the sources and weathering inputs during summer through the river stream.

Conclusion

The present study summarizes the seasonal fluctuations in various physico-chemical parameters in the coastal waters off the Devi estuary as exploratory statistical data output. Freshwater discharge through the river and rivulets includes additions of PO_4-P and SiO_4-Si to the coastal water and is marked during both the seasons. The addition of nitrogenous species (NO_3-N and NO_2-N) from anthropogenic sources such as fertilizer output, as an effect of industrialization in the northern region of the Devi estuary, has been observed during winter in the water near the mouth of the Devi estuary. The interrelationship between varifactors suggests the association of inorganic nutrients during winter. The observed loadings of nitrogenous species to the near-shore coastal water off the Devi estuary being much less during summer relative to that during winter, suggests well-oxygenated condition of the water in summer.

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