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STATISTICAL EVALUATION OF WATER QUALITY PARAMETERS FOR TWO DIFFERENT SEASONS IN MAHI ESTUARY, WEST COAST OF INDIA

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Abstract

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Monthly and seasonal field sampling was conducted to characterize the variations in water column nutrients along four stations in the Mahi estuary, west coast of India from July 2008 to June 2009. Water samples from five stations were studied, from which Stations 1 and 2 are contaminated with effluents released by surrounding industrial complexes. The samples were analyzed for temperature and pH in-situ, and salinity, alkalinity, dissolved oxygen, BOD, sulfate, nitrite, nitrate, total nitrogen, silicate-silicon, phosphate and calcium and magnesium, as per standard methods. The results showed an increased content of sulfate, nitrate, and total nitrogen in both Stations 1 and 2. The entire data has been factorized using principal component analysis to extract total variability and linear relationships for a set of different physico-chemical parameters of the Mahi estuarine system. The results revealed that all the physico-chemical processes depend on the seasonal fluctuations in freshwater input and sea-water intrusion. Cluster analysis was carried out for station-wise average values to understand the relationships between stations. Eigen values showed that PC1 was the most significant component, representing more than 90% of the variance in water quality parameters in the Mahi estuary for both monsoon and non-monsoon seasons. The results showed high deterioration in the physico-chemical quality of water during the non-monsoon season compared to that in the monsoon season.

Key words: Dissolved nutrients, cluster analysis, principal component analysis, seasonal variation.

Introduction

The distribution and behaviour of nutrients in the coastal environment, particularly in the near-shore waters and estuaries, exhibit considerable variations depending upon the local conditions such as rainfall, the quantum of fresh water inflow, tidal incursion and also biological activities including phytoplankton uptake and regeneration. Considering the importance of the role of physico-chemical parameters on the productivity potential of coastal waters, numerous studies pertaining to this have been made in the coastal waters of India to evaluate their seasonal and spatial behaviour (Jayaraman, 1951, 1954; Ramamirtham, Patil, 1964; Sankaranarayana, Reddy, 1968; Naqvi et al., 1978; Rajendran et al., 1980; Panigrahy et al., 1984; Sasmal et al., 1986; Choudhary, Panigrahy, 1991) and their impacts on the occurrence and abundance of phytoplankton populations (Varshney et al., 1983; Prasannakumar et al., 2000; Madhupratap et al., 2001; Sasmal et al., 2005).

During the last century, great concern and attention have been given to the impact of human activities on the integrity and sustainability of coastal ecosystems (Hopkinson, Vallino, 1995; Philips et al., 2004). Monitoring activities of coastal ecosystems have acquired great importance for better understanding of the past processes, present patterns, and future trajectories in aquatic health (Nirmal Kumar et al., 2009; Buzelli et al., 2004). Interpretation of spatially and temporally dynamic coastal biogeochemical patterns which result from a variety of biotic and abiotic factors is a complex task. Analysis of patterns and relationships among water quality parameters is required to understand both external driving forces and the internal estuarine processes. These concerns have focused attention on the need to develop the capability to predict the impact of environmental changes on the structure and function of aquatic ecosystems.

Analysis of multivariate data, which consists of many different attributes or variables recorded for each observation, plays a key role in data analysis (Mazlum et al., 1999; Perez, Valiente, 2005). As it is hard to visualize multi-dimensional space, principal component analysis (PCA), a popular multivariate technique, is mainly used to reduce the dimensionality of multivariate attributes to two or three which can be displayed graphically, with a minimal loss of information (Zhou et al., 2007). PCA summarizes the variation in a correlated multi--attribute to a set of uncorrelated components that comprise principal components (PCs), each of which is a particular linear combination of the original variables and is estimated from the eigenvalues of the covariance or correlation matrix of the original values. PCs provide information on the most meaningful parameters, and describe a complete data set affording data reduction with minimum loss of original information (Shrestha, Kazama, 2007).

The Mahi estuary is one of the largest estuarine systems on the Gulf of Cambay in Gujarat, India, attracting pilgrims from all parts of the country. This estuary is being polluted at Stations 1 and 2 by many industrial effluents from the Vadodara industrial complexes. In this investigation, an attempt has been made to determine the physico-chemical and biological aspects of estuarine water, and to evaluate the effects of effluent and freshwater inflow on the Mahi estuarine system's ecology using a statistical approach.

Material and methods

Study area

The Mahi estuary is a permanent tropical estuary and one of the major estuaries on the Gulf of Cambay, west coast of Gujarat in India (Fig. 1). The estuary is situated at Latitude 22°17´ N and Longitude 72°13´ E. The Mahi river has a length of 800 kms and a total basin of 1,036,200 km2. After traversing the Panch Mahal, Vadodara and Charotar plains, it joins the northern part of the Gulf of Khambhat near Camboi at Kavi, forming a broad estuarine stretch extending to Mohammadpura, approximately 50 km inland. Along its course, the river receives industrial effluents released from many chemical and fertilizer industries in and around the Vadodara industrial area. This is the major source of pollution into the estuary. This estuarine region experiences high, semi-diurnal tides with a range of 5.5 m in spring decreasing to 2.3 m 25 kms upstream and 2.3 m at neap receding to 0.4 m 25 km within the estuary. Salinity intrusion is largely governed by the tidal phase and is noted up to 65 kms upstream during the dry season. Strong tidal currents exceeding 1m sweep the shallow estuary, making it vertically well mixed, except during short periods when the tide slackens (Qasim, 2003).

Five different study sites were selected on the northern and southern banks of the river. Station 1 experiences typical marine conditions at the mouth of the estuary, while Station 2 is located 6 kms downstream where the industrial effluents are mainly discharged. Stations 3, 4 and 5 are located 10, 15 and 20 kms upstream from station 1, respectively.

Sample collection and analysis

Water samples from all five stations of the estuary were collected at monthly intervals for monsoon and non-monsoon seasons from July 2008 to June 2009, using a clean bucket, and bottom water was collected by a Niskin water sampler. Measurements of temperature, pH and dissolved oxygen (DO) were made in the field at the time of sample collection. Water for analysis of all other parameters was collected in a clean Polythene bottle and then transported to the laboratory under refrigeration. Winkler's titrimetric method (Grasshoff et al., 1983) was followed for estimation of DO, salinity was established by Knudsen's method (Grasshoff et al., 1983), alkalinity by the titrimetric method, nitrate by the cadmium reduction method, and phosphate and silica by the ascorbic acid and molybdosilicate methods respectively; all as described by APHA (1998). Sodium and potassium were estimated using flame photometry. Chlorophyll-a was determined by filtering the sample through glass fiber filter papers, extracted in 90% acetone and then estimated spectrophotometrically (APHA, 1998). The data quality was ensured through careful standardization, procedural blank measurements and spike and duplicate samples. The parameters obtained from the laboratory analysis were used as variable inputs for correlation matrix, cluster analysis and for Principal Components Analysis (PCA), which were performed using the SPSS package.

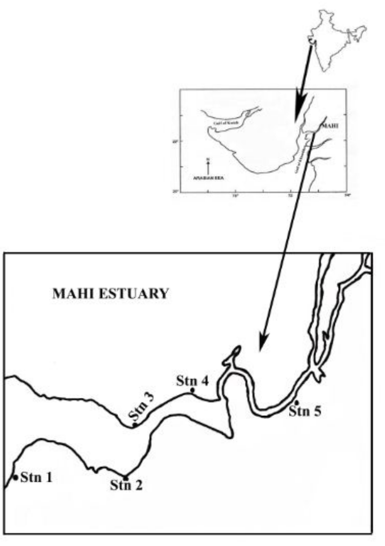

Fig. 1. Map of Mahi estuary showing sampling locations.

Results and discussion

Nutrient status

Descriptive statistics of physico-chemical parameters of water samples from the monsoon and non-monsoon seasons, including minimum and maximum values, mean values and statistical evaluations, involving Standard Error (SE) and Standard Deviation (SD) of the hydrological parameters of Mahi estuary, is presented in Table 1. Description of the correlation matrix of water samples is presented in Tables 2 and 3, and average values for seasonal variation in water quality parameters are illustrated in column graphs in Figures 2a–2j. The majority of the parameters reveal significant seasonal and station-wise concentration variation. The average water temperature in the five stations varied from 26.19 °C to 35.16 °C (Fig. 2a), and water pH was higher during the non-monsoon than the monsoon, varying from 7.16 at Station 4 to 8.81 at Station 1 (Fig. 2b). Salinity showed remarkable seasonal variation with high values in the non-monsoon season. The salinity varied from 0.96 ppt at Station 4 during monsoon to 35.82 ppt at Station 1 during the non-monsoon (Fig. 2c). The freshwater inflow imparted significant influence on lowering salinity during monsoon, while seawater influx exhibited overall control of high salinity values in the non-monsoon period.

During monsoon, DO varied between 2.71 and 9.82 mgL^{-1}, while in non-monsoon it ranged between 0.02 and 4.63 mgL^{-1} (Fig. 2d). Low DO values observed during non-monsoon, particularly at Stations 1 and 2, are most likely due to the increased organic inputs from the industrial effluents (Sankaranarayanan, Qasim, 1969). Biological oxygen demand (BOD) varied widely during seasons; from 2.19 to 19.21 mgL^{-1} during monsoon to 2.38 to

T a b l e 1. Descriptive statistics of physico-chemical parameters of water in the two seasons; monsoon and non--monsoon.

Parameter	monsoon					Non-monsoon				
	Minimum	Maximum	Mean	S.E.M.	S.D.	Minimum	Maximum	Mean	S.E.M.	S.D.
Temperature, °C	26.19	31.67	29.77	0.98	2.20	29.20	35.16	33.03	1.08	2.43
pH	7.16	8.81	8.15	0.29	0.65	7.42	8.72	8.17	0.24	0.53
Salinity, g kg^{-1}	0.96	33.42	24.75	6.12	13.68	3.59	35.82	27.19	6.01	13.44
Alkalinity, mg L^{-1}	72.27	119.35	88.08	8.45	18.90	81.25	197.21	109.37	22.13	49.48
DO, mg L^{-1}	2.71	9.82	5.02	1.27	2.85	0.02	4.63	1.45	0.92	2.05
BOD, mg L^{-1}	2.19	19.21	13.28	3.04	6.79	2.38	28.31	18.52	4.88	10.92
Sulfate, mg L^{-1}	32.68	3198.39	2065.17	565.85	1265.28	91.28	3810.82	2612.78	697.45	1559.54
Nitrite, μg L^{-1}	0.92	139.24	71.87	25.04	55.99	2.71	162.91	108.74	30.09	67.28
Nitrate, μg L^{-1}	2.17	1732.89	919.04	306.38	685.08	417.15	2713.28	1730.02	472.91	1057.45
Total nitrogen, μg L^{-1}	27.13	2184.15	1417.05	440.01	983.88	32.82	2619.14	1696.61	519.33	1161.26
Silicate-silicon, μg L^{-1}	1239.41	10331.37	4821.62	2032.87	4545.63	1302.47	18810.43	7599.99	3648.06	8157.32
Phosphate, μg L^{-1}	12.36	402.57	268.61	76.28	170.57	83.37	832.18	512.09	164.73	368.34
Calcium, mg L^{-1}	3.28	528.31	322.26	106.25	237.58	18.22	591.43	393.96	109.04	243.82
Magnesium, mg L^{-1}	1.73	931.32	701.07	176.63	394.95	7.49	1392.83	818.08	228.56	511.07

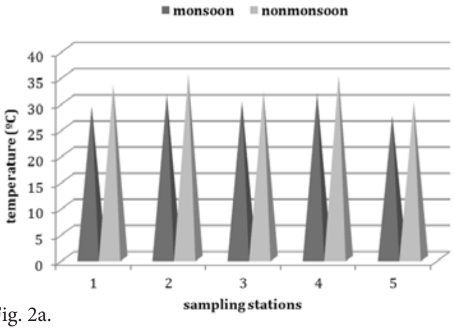

Fig. 2a.

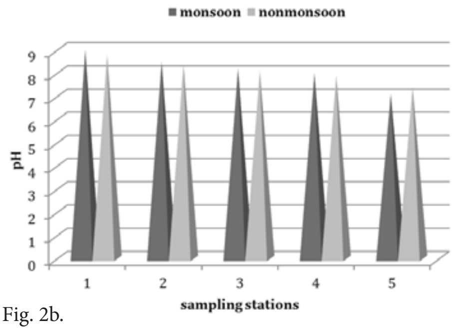

Fig. 2b.

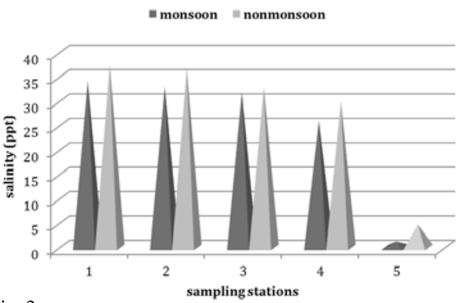

Fig. 2c.

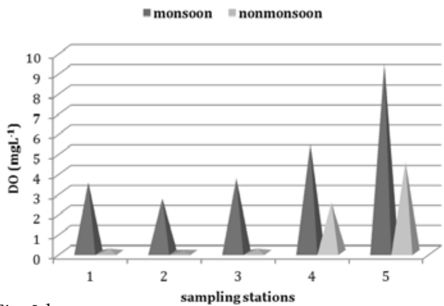

Fig. 2d.

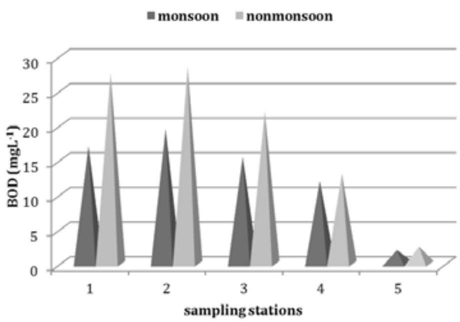

Fig. 2e.

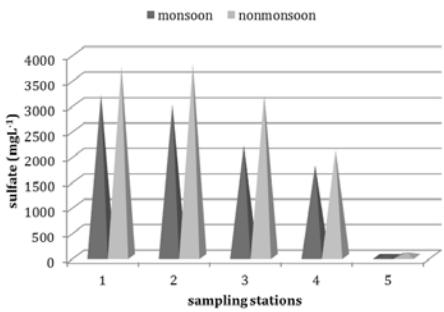

Fig. 2f.

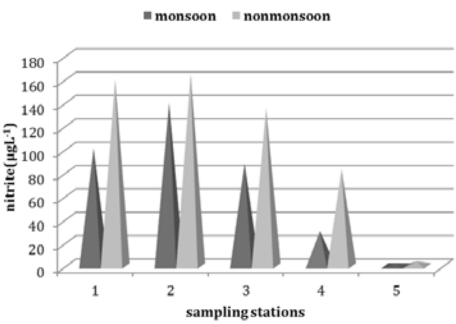

Fig. 2g.

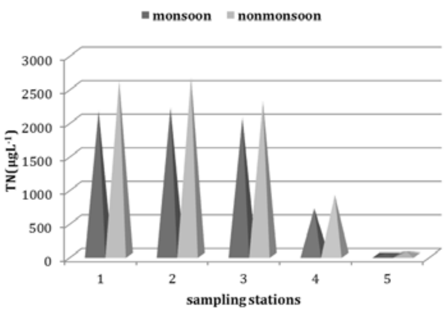

Fig. 2h.

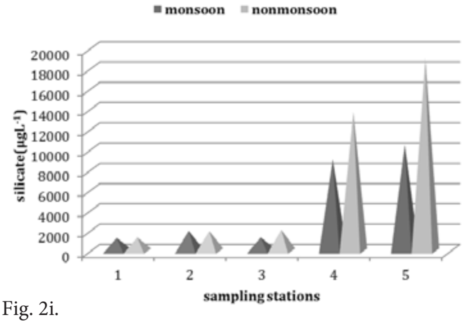

Fig. 2i.

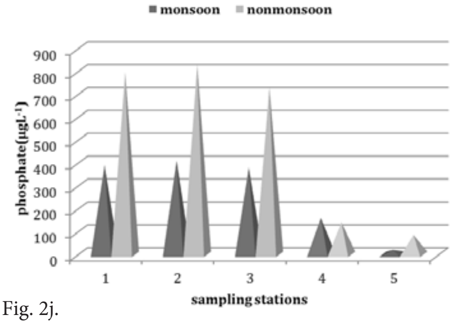

Fig. 2j.

Fig. 2a-2j. Graph showing variation in concentration of different water quality parameters at different sampling locations.

T a b l e 2. Correlation matrix among the physico-chemical parameters of water samples–in the monsoon season.

	Temp.	pH	Salinity	HCO_3	DO	BOD	SO_4	NO_2-N	NO_3-N	TN	SiO_4-Si	P	Ca	Mg
Temp.	1.00													
pH	0.63	1.00												
Salinity	0.82	0.94	1.00											
HCO_3	-0.71	-0.92	-0.97	1.00										
DO	-0.81	-0.96	-0.99	0.95	1.00									
BOD	0.77	0.96	0.98	-0.94	-1.00	1.00								
SO_4	0.72	0.99	0.96	-0.91	-0.98	0.98	1.00							
NO_2—N	0.56	0.91	0.84	-0.81	-0.90	0.93	0.90	1.00						
NO_3—N	0.61	0.93	0.86	-0.82	-0.93	0.95	0.93	1.00	1.00					
TN	0.56	0.95	0.91	-0.93	-0.94	0.96	0.93	0.96	0.95	1.00				
SiO_4—Si	-0.40	-0.90	-0.83	0.88	0.85	-0.88	-0.85	-0.92	-0.90	-0.98	1.00			
P	0.64	0.96	0.94	-0.95	-0.96	0.98	0.95	0.95	0.95	1.00	-0.96	1.00		
Ca	0.51	0.96	0.88	-0.89	-0.92	0.94	0.94	0.96	0.96	0.99	-0.98	0.98	1.00	
Mg	0.85	0.92	1.00	-0.96	-0.97	0.96	0.94	0.79	0.82	0.87	-0.77	0.90	0.84	1.00

28.31 mgL^{-1} in the non-monsoon. Here, the higher values were recorded in samples collected from the vicinity of point sources of pollution (Fig. 2e). The sulfate varied from 32.68 mgL^{-1} in the monsoon to 3810.82 mgL^{-1} in the non-monsoon (Fig. 2f). Nutrient species of nitrogen (N) such as nitrate (Fig. 2g) and nitrite were recorded (Table 1;); where Nitrite-N (NO_2—N) effected the least seasonal difference, while concentrations of nitrate-N (NO_3—N) were higher in the non-monsoon season than during monsoon. Similarly, the total nitrogen (TN) also recorded high values during the non-monsoon period compared to the monsoon (Fig. 2h). Silicate concentration varied from 1239.41 to 10331.37 μg L^{-1} during monsoon and from 1302.47 to 18810.43 μg L^{-1} in the non-monsoon (Fig. 2i). The phosphate values

T a b l e 3. Correlation matrix among the physico-chemical parameters of water samples — in the non-monsoon season.

	Temp.	pH	Salinity	HCO_3	DO	BOD	SO_4	NO_2-N	NO_3-N	TN	SiO_4-Si	P	Ca	Mg
Temp.	1.00													
pH	0.73	1.00												
Salinity	0.87	0.89	1.00											
HCO_3	-0.88	-0.86	-1.00	1.00										
DO	-0.68	-0.93	-0.93	0.91	1.00									
BOD	0.72	0.98	0.92	-0.89	-0.98	1.00								
SO_4	0.78	0.97	0.97	-0.95	-0.98	0.99	1.00							
NO_2—N	0.75	0.97	0.95	-0.93	-0.99	0.99	1.00	1.00						
NO_3—N	0.58	0.97	0.82	-0.78	-0.94	0.98	0.94	0.95	1.00					
TN	0.63	0.95	0.89	-0.86	-0.99	0.99	0.97	0.98	0.98	1.00				
SiO_4—Si	-0.56	-0.93	-0.86	0.83	0.98	-0.97	-0.95	-0.97	-0.97	-1.00	1.00			
P	0.47	0.91	0.77	-0.73	-0.94	0.95	0.90	0.92	0.98	0.97	-0.98	1.00		
Ca	0.73	0.97	0.94	-0.92	-0.99	1.00	1.00	1.00	0.96	0.99	-0.97	0.94	1.00	
Mg	0.74	0.95	0.95	-0.93	-0.93	0.93	0.96	0.95	0.88	0.91	-0.89	0.82	0.95	1.00

varied between 12.36 μg L^{-1} to 402.57 μg L^{-1} during monsoon, and ranged from 83.37 μg L^{-1} to 832.18 μg L^{-1} during non-monsoon (Fig. 2j). While the major sources of phosphate were domestic sewage and industrial and agricultural effluents (Babu et al., 2000; Madramootoo et al., 1997), the highest value of phosphate observed at Station 2 is considered to be caused by the discharge of industrial effluents from Vadodara.

Correlation analysis

The water quality data is interpreted by correlation matrix, PCA and cluster analysis. The correlation matrix of 14 variables in the monsoon and non-monsoon seasons is given in Tables 2 and 3. During monsoon, salinity, pH, bicarbonate (HCO_3), sulfate (SO_4), calcium (Ca) and magnesium (Mg) are positively correlated with each other. Influx of freshwater is high during this season, which induces a negative impact on tidal effects as a source of anions. Reduced concentration in these ions negatively affected concentrations, and also hardness, pH and salinity during this season. Although negative correlation of nutrients was observed with pH, sulfate and salinity, nutrients varied positively with BOD. The positive correlation of sulfate with Ca and Mg indicated the influence of tidal waters on these elements. During the non-monsoon season, salinity, pH, sulfate, Ca and Mg showed the same trend as in monsoon. Silicate was negatively correlated with Ca and Mg, and the reverse was true for SO_4.

Principal component analysis

The data quality for factor analysis was confirmed by the Kaiser–Meyer–Olkin (KMO) test (Shrestha, Kazama, 2007). The correlation matrix was used in PCA (Barbieri et al., 1999), together with the covariance matrix. PCA of the water quality data developed four principal components (PC) as seen from the Eigen values in Tables 4 and 5). This explains 100% of the variability for both the monsoon and non-monsoon seasons. During monsoon, PC1 accounted for 90.211% of the total variance, where positive factor loadings were observed for all parameters except HCO_3, DO, and SiO_4—Si. During the non-monsoon season, PC1 accounted for 91.506% of total variance, where positive factor loadings were recorded for all parameters except HCO_3, DO, and SiO_4—Si. Positive PC2 loading was registered for temperature, salinity, BOD, SO_4, SiO_4—Si and Mg, and this accounted for 6.857% of the total variability in monsoon season and 6.495% of total variability during the non-monsoon. PC3, which contributed 2.005% of the total variability during monsoon and 1.205% of the total variability in non-monsoon, was positively loaded with temperature, HCO_3, BOD, SO_4, NO_2—N, NO_{3-}—N, and SiO_4—Si. The contribution of PC4 to the total variability was 0.926% during monsoon and 0.792% for the non-monsoon period. SO_4 was the only parameter positively loaded in all the PCs during the monsoon season. Meanwhile, the negative relationship between nutrients and DO observed in the PCA may have been due to consumption of large amounts of oxygen by organic matter, especially in the non-monsoon season (Singh et al., 2005).

T a b l e 4. Factor analysis and factor loadings of principal components (PCs) in Mahi estuary- in the monsoon season.

% of variance	90.211	6.857	2.005	0.926
Cumulative (%)	90.211	97.069	99.074	100
Eigen values	12.630	0.960	0.281	0.130
PC	PC1	PC2	PC3	PC4
Temp.	0.715	0.671	0.164	-0.111
pH	0.976	-0.060	-0.038	0.207
Salinity	0.972	0.211	-0.099	0.024
HCO_3	-0.953	-0.101	0.273	0.086
DO	-0.989	-0.144	-0.034	-0.005
BOD	0.996	0.069	0.058	-0.004
SO_4	0.979	0.052	0.034	0.194
NO_2—N	0.938	-0.233	0.248	-0.069
NO_3—N	0.952	-0.170	0.255	-0.004
TN	0.976	-0.200	-0.043	-0.068
SiO_4—Si	-0.917	0.360	0.136	0.106
P	0.990	-0.111	-0.038	-0.080
Ca	0.965	-0.262	-0.005	0.026
Mg	0.946	0.300	-0.121	0.031

T a b l e 5. Factor analysis and factor loadings of principal components (PCs) in Mahi estuary — in the non-monsoon season.

% of variance	91.506	6.495	1.205	0.792
Cumulative (%)	91.506	98.002	99.207	100
Eigen values	12.811	0.909	0.169	0.111
PC	PC1	PC2	PC3	PC4
Temp.	0.748	0.627	0.187	-0.109
pH	0.974	-0.037	0.188	0.120
Salinity	0.951	0.283	-0.121	0.003
HCO_3	-0.929	-0.335	0.155	0.017
DO	-0.987	0.071	0.129	0.060
BOD	0.994	-0.070	0.080	-0.022
SO_4	0.998	0.055	-0.015	-0.008
NO_2—N	1.000	0.002	-0.005	-0.027
NO_3—N	0.954	-0.259	0.153	0.005
TN	0.984	-0.171	-0.030	-0.042
SiO_4—Si	-0.965	0.243	0.094	0.029
P	0.923	-0.375	0.027	-0.081
Ca	0.999	-0.039	0.003	-0.021
Mg	0.957	0.107	-0.050	0.264

Cluster analysis

Cluster analysis for both seasons was performed for station-wise average values, in order to clarify the relationship between different stations. Water quality parameters of the stations for the monsoon season formed mixed clusters (Fig. 3), where those formed by,Stations 1 to 3 behaved in a similar manner, while Stations 4 and 5 behaved individually. Water quality parameters of the stations during the non-monsoon formed two clusters. The first was formed by Stations 1, 2 and 3 which received high loadings of effluents, so their water quality behaved similarly, while the second cluster was formed by Stations 4 and 5 which received a continuous flow of fresh water.

Conclusion

The present study summarizes the seasonal fluctuations in various physico-chemical parameters in the coastal waters of the Mahi estuary as exploratory statistical data output. It is inferred that the nutrient concentration in the estuary has been regulated by the freshwater inflow and also by tidal mixing. PCA and cluster analysis showed that very little freshwater input during the non-monsoon season and high nutrient input from sources other than

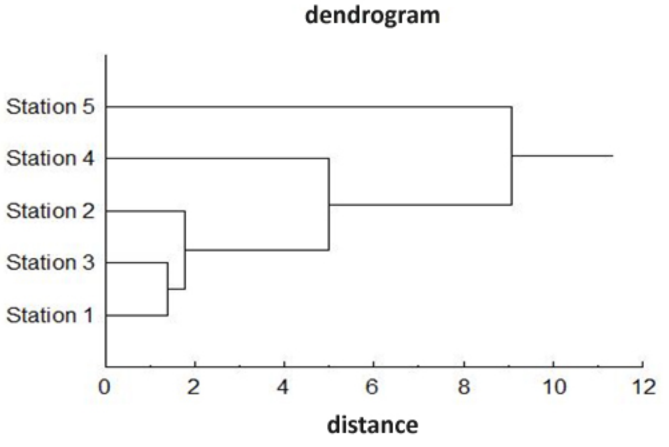

Fig. 3a. Dendrogram showing clusters formed by samples at various stations during monsoon season.

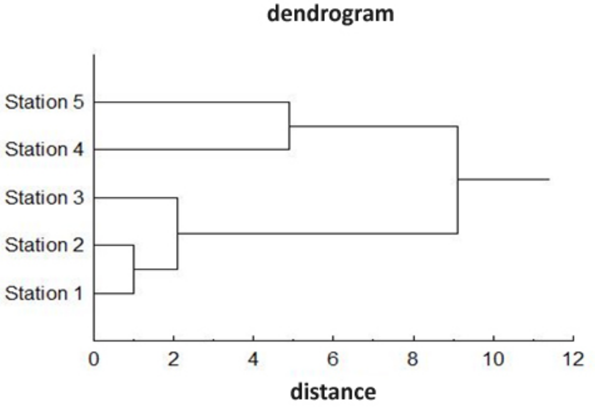

Fig. 3b. Dendrogram showing clusters formed by samples at various stations during non-monsoon season.

freshwater, such as sewage and industrial discharges and other point sources of pollution, have caused localized problems to the water quality of the Mahi estuary. The highest concentrations for all nutrients except DO were observed during the non-monsoon. Distribution of dissolved inorganic nutrients in this tropical coast is very heavily influenced by factors including tidal fluctuations, physical stirring by currents (Bowman, 1977), by benthic invertebrates (Hammond et al., 1977; McCaffery et al., 1980) and by drainage discharged from industries and cities around the estuarine zone. A significant increase in nitrate, phosphate, and silicate, and conversely a decrease in DO, were observed during this study. Cluster analysis proved a clear variation in water quality at the different stations. Variability among different components was described by PCA, and this determined that PC1 is responsible for much of the variation existing in this zone during the study period.

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