

Evaluation of surface water and sediment quality in Chicalim Bay, Nerul Creek and Chapora Bay from Goa Coast, India—a statistical approach

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Abstract

To better understand the spatial and temporal variation in surface water and sediment quality parameters were evaluated from the three sites Chicalim Bay (CB), Nerul Creek (NC) and Chapora Bay (ChB) along the Goa coast, which has major oyster beds. Multivariate analysis such as cluster analysis (CA), Box–Whisker–plot (box plot) and principle component analysis (PCA) revealed that nitrate (NO₃-N), nitrite (NO₂-N), phosphate (PO₄-P), particulate organic carbon (POC), total suspended solids (TSS), dissolved oxygen (DO) and phaeopigments are the responsible parameters for spatio-temporal variability among the studied sites. Results showed an elevated level of ecotoxicological hazard at CB while moderate toxicological risks were observed for organisms at NC. In contrast, ChB was considerably pristine compared to other two sampling sites. Results of present study showed marked dominance of nutrients, phaeopigments, POC and TSS at CB and NC. The increased levels of these parameters are attributed to the anthropogenic activities which may cause potential risk to humans via consumption of oysters. Therefore, we suggest monitoring heavy metal concentrations in tissue of commercially important oyster species and their ambient environment (water and sediment) from these estuaries is necessary to create a comprehensive pollution database.

Keywords Environment quality, Oyster beds, Anthropogenic activities, Multivariate analysis, Estuaries

Introduction

Estuaries and coastal ecosystems are among the most valuable and yet highly vulnerable habitats in the world (Jickells 1998). These ecosystems are increasingly becoming threatened due to growing population and exploitation pressure in most parts of the world. Estuaries and coastal ecosystems have greater biodiversity than open ocean regions and are one of the most exploited ecosystems in the world (Blaber 2000). The health of coastal systems of India is being deteriorated due to the rapid introduction of pollutants of physical, chemical and biological origin, resulting from various anthropogenic activities (Qasim and Kureishy 1986). These pollutants act unfavorably to the aquatic organisms and change their biodiversity and alter the characteristics of the ecosystem (Hall 1985; House 1993).

Goa is situated along the central west coast of India between 14°49' and 15°42' N and 73°38' and 73°24' E. It has ~105 km coastline intended with bays, creeks, promontories, sea cliffs, estuaries and world famous beaches. Nine rivers (Terekhol, Chapora, Baga, Mandovi, Zuari, Sal, Saleri, Talpona and Galgibag) flow across the state which drains into the Arabian Sea. Out of these, Mandovi and Zuari rivers are famous as lifeline of Goa because of their economic importance which covers the 69% of the geographic area of the state. In Goa, estuaries are used for ore transport, fishing, tourism activities, aquaculture, harbour development and waste disposal. Such anthropogenic activities may alter the physical, biological and geochemical conditions of the estuarine system to a considerable extent. Coastal areas also get pressurized by increasing human population for resource utilization which leads to habitat degradation, fragmentation and destruction (Gray 1997). Moreover, these estuaries are classified as a "monsoonal estuaries" (Shetye et al. 2007; Vijith et al. 2009), which receives abundant river discharge only during the monsoon and negligible discharge during the non-monsoon period. Edible bivalves, particularly *Crassostrea gryphoides*, *Crassostrea madrasensis*, *Saccostrea cucullata*, *Paphia malabarica*, *Meretrix casta*, and *Villorita cyprynoides* are exploited round the year in Goa. They are confined to the shallow and intertidal regions of estuaries in close vicinity to or in regions influenced by different anthropogenic activity. Population densities of oyster *Crassostrea* spp. were found along the Goa coast in the range of 100–630 individuals/m² (Jagtap et al. 2011). Their beds were most predominant in Chapora and Mandovi estuaries in North Goa and Zuari and Talpan estuaries in South Goa. Therefore, it is essential to regularly monitor the ambient environment (surface water and sediment) of oyster species.

To understand the estuarine health status some measures of reference physico-chemical parameters is often necessary. Due to complexity of relationship and interdependence of key environmental

factors, it is difficult to draw a clear conclusion directly. However, statistical analysis can extract the underlying information and explain the structure of data in detail. In recent years, multivariate statistical techniques have been successfully applied to evaluate spatio-temporal variations of physico-chemical parameters caused by natural and anthropogenic factors in coastal waters (Simeonov et al. 2004; Singh et al. 2004; Panda et al. 2006; Shirodkar et al. 2009; Wu et al. 2010; Sahu et al. 2013; Jha et al. 2014).

In the present study, we have used this technique to explain the influence of possible sources (natural and anthropogenic) on water and sediment quality of Chicalim Bay, Nerul Creek and Chapora Bay from the Goa coast.

Materials and methods

Study area

Based upon occurrence of major oyster beds which are subjected to different anthropogenic activities, three different sites were chosen from the Goa coast, India (Fig. 1). The details of selected sites are as follows:

Chicalim Bay (CB) ($15^{\circ}24'3.52''$ N, $73^{\circ}51'14.24''$ E) is located on the southern bank towards confluence of Zuari. This site hosts various shipbuilding industries, yards, workshops and recreational anthropogenic activities. This site is also exposed to iron ores transportations.

Nerul Creek (NC) ($15^{\circ}30'37.70''$ N, $73^{\circ}46'48.75''$ E) opens into the Aguada Bay of Mandovi estuary and extends inside the land in U-shape up to a length of about ~8.5 km. This site is influenced by restaurants discharge, fishing and other tourism activities and is also exposed to iron ores transportations from mines located upstream.

Chapora Bay (ChB) ($15^{\circ}36'30.43''$ N, $73^{\circ}44'7.19''$ E) site is located far from main city. This site is exposed to major fish landing jetty, sewage disposal from land inhabitant along the bank of river.

Sample collection and analysis

Monthly sampling for a period of 14 months (April 2013–May 2014) was carried out at CB and NC. However, at ChB which was considered as a relatively pristine area, samplings was done once in four months covering three seasons viz. monsoon (July 2013), post-monsoon (November 2013) and pre-monsoon (March 2014). Surface water and sediment samples were collected from the above-mentioned sites and brought to the laboratory in an ice box for hydrological and geochemical parameters analysis. All the samples were analyzed in duplicates.

Climatological Data

The monthly average data of atmospheric temperature, humidity and rainfall for study period were obtained from the Autonomous Weather Station (AWS) installed at the National Institute of Oceanography (NIO), Dona Paula, Goa.

Water analysis

Temperature and pH were measured on site using calibrated thermometer and a portable pH meter, respectively. Salinity was determined by a refractometer (ATAGO, S/Milli-E). The samples for dissolved oxygen (DO) were fixed on site and later analyzed according to Winkler's procedure (Parsons et al. 1984). For estimation of chlorophyll *a* (Chl *a*) and phaeopigment, 500 ml of surface water was filtered through the Whatman GF/F filter paper. The pigments were extracted in 90% acetone (10 ml) for 24 h at 4°C. Fluorescence was measured before and after acidification with two drops of 1.2 N HCl following the JGOFS protocol (UNESCO, 1994). Nutrients such as nitrate (NO₃-N), nitrite (NO₂-N) and phosphate (PO₄-P), particulate organic carbon (POC) were analyzed by following Parsons et al. (1984) method. Total suspended solids (TSS) in water samples (500 ml) were filtered through a pre-weighed 0.45 µm Millipore membrane filter paper. The residue on the filters was dried at 60 °C till constant weight was obtained. The difference between initial and final weight of residue was recorded. Results of TSS (dry weight) were expressed in mg/L as described by Reddy et al. (1994).

Sediment analysis

For measurement of total organic carbon (TOC), sediment samples were decalcified using 1N HCl, washed thoroughly with deionized water, and dried at 60 °C. The total carbon (TC) and total nitrogen (TN) was analyzed without acid treatment. Following that concentration of TOC, TC and TN were measured using an elemental analyzer (Flash EA 1112 series, Thermo Fisher Scientific) and values were expressed in percentage. For texture analysis, sediment samples were desalinated by washing repeatedly with deionized water and dried at 45 °C. Dried sediment samples (15 g) were first disaggregated using 10% hexametaphosphate and then treated with 30% H₂O₂ for removal of organic matter. The sample was put through a 63 µm sieve (USA standard testing sieve, A.S.T.M.) to separate the sand fraction from the bulk sediment and was oven dried at constant temperature 60 °C and weighed to calculate sand fraction percentage. The remaining mud (silt+clay) fraction from the same was analyzed by laser size particle analyzer (Malvern Mastersizer 2000). The data are presented as weight percentage (wt %) in this study.

Statistical analysis

The basic statistics were applied on raw data set. The mean \pm standard deviation (SD), maximum and minimum values of surface water and sediment parameters were taken separately for each site using Microsoft Office Excel 2007. Pearson's correlation test was used to assess the significance of association between environmental parameters at each site. To determine the significance of spatial and temporal variation in water and sediment parameters, two way ANOVA was used. Further statistical analysis applied only on surface water parameters as the sediment parameters did not show much significant variation in the two way ANOVA analysis. Hereafter, values of surface water parameters at CB and NC were taken as an average of four months in each seasons Monsoon (Mon: June–September); Post-monsoon (PostM: October–January); Pre-monsoon2 (PreM2: February–May, 2014 except pre-monsoon1 (PreM1: April–May, 2013). To minimize the effects of differences in measurement units and to deliver the data dimensionless all the water variables values were normalized. Cluster analysis (CA), principle component analysis (PCA) performed on normalized data. Based on CA, raw data were examined using Box–and–Whisker plots. All statistical computations were made using STATISTICA 8 (StatSoft, Inc., USA) and PRIMER 6 (Primer-E Ltd., Plymouth, UK) software.

Results and Discussion

The climate of Goa is generally tropical with humid conditions. During the study period, the atmospheric temperature ranged from 25.5 to 29 °C. The average humidity of ambient atmosphere reached up to 77 %. The total rainfall received during the study period at Goa coast was about 7501 mm (Fig. 2).

Environmental conditions such as temperature, pH, salinity, food availability, nutrient levels, suspended load etc. have considerable impact on the physiology of sedentary, filter feeder oyster species (Lenihan 1999). Therefore, in the present study attempt has been made to decide the suitability of a site for oyster consumption from these regions by measuring the environmental variables. The annual mean \pm SD with minimum and maximum values recorded for each of the measured variables from sampling sites are shown in Table 1. Under hydrological observations, the surface water temperature observed within the normal tropical ocean ranged between 28 °C and 29.4 °C. However, lowest values of pH and salinity were observed during monsoon compared to non-monsoon period at all the three sites. Increased rainfall and dilution of seawater by the freshwater influx led to decreased salinity (1–2 PSU) in surface water. During monsoon heavy land runoff contribute large amount of organic material forming organic acids due to decomposition, which may

be one of the reasons responsible to decrease in pH at all the three sites. James and Najmuddin (1986) also observed similar phenomenon in Palk Bay, Mandapam. During monthly observations, relatively higher concentrations of DO, Chl *a*, and phaeopigments were observed at CB than NC. Dissolved oxygen showed biologically stressful levels (hypoxic threshold) in some pre-monsoon months with minimum values 2.54 mg/l and 2.97 mg/l at CB and NC respectively. Further, NO₃-N, NO₂-N, PO₄-P, POC and TSS were found higher at site CB. In sediment analysis, mean value of sand percentage (98.3%) was found to be higher whereas TOC (0.11%) and TC (0.18%) were very low at ChB among the three sites. This low carbon content could be attributed to the dominant sandy nature of the sediment. Comparatively higher average value of TOC (1.36%) and TC (1.59%) of sediment were observed at NC, though percentage of clay is less compared to CB site. This may be attributed to mangrove vegetation at NC which contributed more input of organic material from the catchment area into sediment of the bay. Concentrations of TN were also low in surface sediment at CB (0.01%) and NC (0.03%) whereas at ChB it was below detection limit. Pradhan et al. (2014) also reported low values of TC and TN from Chapora estuary in comparison to Mandovi and Zuari estuaries. Shynu et al. (2015) found similar results of OC (0.24–1.34%) and TN (0.01–0.07%) from Mandovi and Zuari estuaries.

Pearson correlation matrix at the significant level of $p < 0.05$ was applied to uncover the relationship among the ecological status indicators (Table 2–4). At all the three study sites the values of nutrients showed significant negative relationship with temperature, salinity and pH. The reason for this relationship could be the terrestrial runoff containing domestic waste in the waters of study sites. In contrast, at CB a significant positive relationship was observed among POC, chl *a* and phaeopigments (Table 2) suggesting occurrence of productive process resulting in enhancement of the oyster population in this bay. However, this correlation increases the potential health hazard to human as oyster in this bay could assimilate more pollutant (metals, bacteria, etc.) along with food particles. The observed values of TSS showed a significant positive correlation with NO₃-N, PO₄-P, DO and phaeopigments whereas a negative relationship was observed with salinity. This positive correlation indicates that the nutrient and oxygen rich freshwater carries suspended load into the estuary. At NC, POC was negatively correlated with salinity (Table 3). This is attributed to the particulate organic matter which enters the water body along with the freshwater efflux. There is no significant relationship observed between POC and TSS at any of the study sites. Further, the sediment analysis showed a highly significant ($p = 0.000$) positive correlation between TOC and TC at CB as well as at NC. However, a non-significant relationship was observed at ChB (Table 4) which may be attributed to the sandy nature of sediment.

Two way ANOVA was used to test the differences in temporal and spatial variation in parameters (Table 5). The values of ANOVA demonstrated significant differences ($p < 0.05$) among the sites, seasons and a site and season interaction. $\text{NO}_3\text{-N}$, POC and TSS showed a significant ($p < 0.05$) seasonal and site wise variation. However, a non-significant seasonal variation was observed among TOC, TC and TN of sediment.

Cluster analysis was done using Euclidean distance test to detect the similarity in the water samples from three localities in four different seasons. Five distinct groups (Group A: CB Mon; Group B: CB PreM1 and NC PreM1; Group C: NC PreM2, ChB PostM, ChB PreM and NC PostM; Group D: CB PreM2 and CB PostM; Group E: NC Mon and ChB Mon) were formed based on the seasonal variation in the studied sites (Fig. 3). In Group A only CB Mon was present While CB PreM1 and NC PreM1 clustered in another group (Group B). Site CB and NC showed similar characteristics in first pre-monsoon although anthropogenic activities are different at these sites. Group C included NC PreM2, ChB PostM, ChB PreM, and NC PostM. This group showed more similarity between NC and ChB sites in pre- and post-monsoon except during first pre-monsoon (PreM1) at NC. CB PreM2 and CB PostM formed another group (Group D). Overall, site CB formed a two separate clusters such as Group A and Group D in Monsoon and non-monsoon period respectively. Group E comprised of NC Mon and ChB Mon. The data analyzed in present study clearly shows that the monsoon clusters are widely separated from non-monsoon. The reason for the observed disparity between two seasons (monsoon and non-monsoon) could be due to the influence of south-west monsoon on the hydrology of studied water bodies.

Variables responsible for group formation in CA are explained by Box-and-Whisker plots (Fig. 4). From the plots, it is observed that most of the parameters are showing wide ranges of variation in Group A followed by Group E. The reason for the observed variations could be explained by higher influence of land runoff in monsoon period in above-mentioned groups. On other hand, variability in the concentrations of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{PO}_4\text{-P}$, POC and TSS are less in Group C which suggests that in non-monsoon season, NC and ChB site do not show much difference in environmental conditions. Presence of low DO values in PreM1 at CB and NC water bodies was the main responsible factor to differentiate Group B from other groups (Fig. 4 c). However, Group D which is characterized by higher values of phaeopigment, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, POC and TSS indicates poor water quality at CB in pre and post monsoon season. The characteristic values observed at CB could be due to commercial and industrial activities such as fishing, ship building activities and iron ore transportation at this site. These activities enhance turbulence in the water which causes re-suspension of sediment. As a result, this phenomenon increases the phaeopigment levels in water, since the bottom sediments

contain higher quantity of degrading pigments (Anand et al. 2014). The geomorphology of CB may be another reason for the observed values at this site since more ingress of sea water occurs during daily tidal circulations at CB (Selvakumar et al. 1980). Mining rejects is also one of the major sources of NO_3 in the estuaries of Goa (De Sousa 1983).

The PCA approach was used to extract the important driving factors that are responsible for spatial and temporal variations in water quality. Results of PCA analysis are presented in Table 6. Based on the eigenvalue (>1), first three principal components (PCs) were retained as they explained 89.8% of the total variability in the hydrological parameters. Further, comparison between loading and scoring on each PC have helped to identify the relationship between the variables and samples. The PC1 explained 52.1% of the variance and is associated with all nutrients ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$), POC and TSS which showed a negative loading with salinity. The scoring on PC1 showed all the three sites during monsoon were influenced by high concentrations of these parameters. This indicates that all the studied sites (CB, NC and ChB) are affected by nutrient-rich freshwater runoff from land and resuspended fine-grained organic-rich sediments during the monsoon period. Similar results were obtained by other researchers when they evaluated the water quality of estuarine regions of Goa (Sardessai and Sundar 2007; Anand et al. 2014). The second PC (PC2) described 28.5% of the variability and characterized by positive loading of Chl *a*, pH and phaeopigments. Site CB in all the seasons and site NC during PreM1 showed the highest values of Chl *a*, pH and phaeopigments. The third PC (PC3) accounting for 9.2% of the variance is mainly due to positive loading of DO. High loading of DO was observed at all the three sites during PostM period. Additionally, NC and ChB showed strong relationship with DO on PC3 in PreM2 and in PreM, respectively. Variables Chl *a*, pH and DO showed positive correlation on PC2 and PC3 respectively mostly in pre and post monsoon. Generally, these variables are involved in various biological processes, such as photosynthesis, respiration activities and organic matter decomposition etc. (Zang et al. 2011) which also influence the water quality. Similar results were observed in waters samples at CB throughout the year. From the PCA results, it is evident that in all the seasons, site CB is more influenced by land-based anthropogenic activities than other two sites (NC and ChB).

Conclusion

The different physico-chemical parameters measured in present study have been used as an indicator for potential pollution in all the three study sites (CB, NC and ChB). Based on the results of present study we can conclude that CB is most affected by anthropogenic activities while ChB is considerably pristine compared to the other two sampling sites. Further, increasing anthropogenic activities along the banks of Mandovi and Zuari rivers introduce domestic and anthropogenic metals

and cause the contamination in their estuarine regions (Pradhan and Shirodkar 2011). Previous studies had reported the metal contamination in Mandovi (Alagarsamy 2006; Shynu et al. 2013; Veerasingham et al. 2015) and Zuari (Kessarkar et al. 2013) estuaries due to mining and other anthropogenic activities which occurs along the bank of rivers throughout the year. This attracts the urgent need to monitor more parameters such as heavy metal concentrations in water, sediment and associated biota especially commercially important oyster species from these areas to create a comprehensive pollution database.

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Table 1 Physico-chemical parameters (mean \pm SD, min., max.) at all the sites during study period 2013–2014

CB = Chicalim Bay, NC = Nerul Creek, ChB = Chapora Bay, SD = standard deviation, Min. = minimum, Max. = maximum

Parameters	CB				NC				ChB			
	Mean	SD	Min.	Max.	Mean	SD	Min.	Max.	Mean	SD	Min.	Max.
Water parameters												
Temperature (°C)	29.42	2.58	25.00	34.00	28.86	1.73	26.00	32.00	28.00	1.80	26.00	29.50
pH	7.90	0.42	6.75	8.60	7.74	0.60	6.23	8.70	7.45	1.04	6.25	8.10
Salinity (PSU)	24.86	10.62	2.00	34.00	23.26	11.20	1.00	34.00	17.33	13.28	2.00	25.00
DO (mg/l)	5.46	1.21	2.54	7.41	4.87	1.16	2.97	6.58	5.73	0.38	5.36	6.12
Chl <i>a</i> (µg/l)	7.34	3.49	1.33	12.34	4.77	2.30	2.02	8.97	3.10	0.80	2.27	3.87
Phaeopigment	9.85	8.85	3.76	34.03	2.43	1.28	0.73	5.82	1.71	1.19	0.63	2.98
Nitrate (µmol/l)	6.86	9.09	0.94	27.49	3.78	6.48	0.01	24.48	8.39	13.54	0.45	24.02
Nitrite (µmol/l)	0.36	0.24	0.08	0.97	0.28	0.24	0.10	1.04	0.21	0.16	0.11	0.39
Phosphosphate (µmol/l)	2.14	2.61	0.43	9.18	1.14	1.31	0.06	3.96	1.38	1.90	0.21	3.57
POC (µg C/l)	4349.30	2500.17	2061.03	11325.60	2224.60	1668.17	901.45	6773.98	1512.84	347.81	1137.40	1824.08
TSS (mg/l)	239.68	260.72	30.27	870.53	29.96	20.08	11.13	86.07	17.39	21.64	3.70	42.33
Sediment parameters												
Sand (%)	79.49	12.55	57.31	97.04	80.09	6.31	66.19	90.06	98.34	0.97	97.25	99.11
Silt (%)	18.11	11.05	2.43	37.87	17.60	5.49	8.88	29.73	1.51	0.87	0.80	2.49
Clay (%)	2.34	1.54	0.52	5.35	2.29	0.87	1.06	4.08	0.14	0.09	0.09	0.25
TOC (%)	0.85	0.60	0.16	2.05	1.36	0.51	0.54	2.23	0.11	0.03	0.08	0.13
TC (%)	1.39	0.91	0.17	3.57	1.59	0.66	0.64	3.01	0.18	0.10	0.07	0.28
TN (%)	0.01	0.03	0.00	0.12	0.03	0.07	0.00	0.18	0.00	0.00	0.00	0.00

Table 2 Correlation coefficient (r values) between physico-chemical parameters at Chicalim Bay during study period

* Significance (P<0.05) ** Significance (P<0.01) *** Significance (P<0.001)

	Temp.	pH	Salinity	DO	Chl <i>a</i>	Phaeo.	NO ₃ -N	NO ₂ -N	PO ₄ -P	POC	TSS	Sand	Silt	Clay	TOC	TC	TN
Temp.	1																
pH	0.099	1															
Salinity	0.631*	0.245	1														
DO	-0.322	-0.237	-0.532	1													
Chl <i>a</i>	0.325	0.633*	-0.085	0.091	1												
Phaeo.	-0.106	0.309	-0.24	0.215	0.597*	1											
NO ₃ -N	-0.716**	-0.302	-0.966***	0.535*	-0.012	0.181	1										
NO ₂ -N	-0.243	0.265	-0.148	0.116	0.334	0.758**	0.226	1									
PO ₄ -P	-0.467	-0.164	-0.714***	0.255	0.215	0.552*	0.741**	0.563*	1								
POC	-0.368	0.588*	-0.337	0.12	0.567*	0.683**	0.278	0.43	0.271	1							
TSS	-0.479	-0.333	-0.788***	0.588*	0.175	0.633*	0.784***	0.509	0.806***	0.365	1						
Sand	0.057	0.205	-0.385	0.107	0.529	0.301	0.307	-0.07	0.311	0.526	0.279	1					
Silt	-0.06	-0.217	0.382	-0.126	-0.536*	-0.3	-0.302	0.078	-0.297	-0.525	-0.272	-0.999***	1				
Clay	-0.045	-0.127	0.375	-0.005	-0.435	-0.283	-0.325	0.006	-0.387	-0.478	-0.293	-0.966***	0.955***	1			
TOC	-0.057	-0.249	0.344	-0.167	-0.485	-0.328	-0.233	0.064	-0.191	-0.496	-0.24	-0.874***	0.887***	0.767***	1		
TC	-0.052	-0.457	0.253	-0.201	-0.525	-0.342	-0.132	-0.039	-0.073	-0.53	-0.133	-0.729**	0.748**	0.586*	0.929***	1	
TN	-0.047	0.001	0.139	0.004	0.001	-0.142	-0.186	-0.271	-0.178	-0.215	-0.198	-0.405	0.383	0.561*	0.260	0.186	1

Table 3 Correlation coefficient (r values) between physico-chemical parameters at Nerul Creek during study period

	Temp.	pH	Salinity	DO	Chl <i>a</i>	Phaeo.	NO ₃ -N	NO ₂ -N	PO ₄ -P	POC	TSS	Sand	Silt	Clay	TOC	TC	TN
Temp.	1																
pH	0.379	1															
Salinity	0.469	0.507	1														
DO	-0.28	0.185	-0.4	1													
Chl <i>a</i>	0.09	-0.507	-0.31	-0.509	1												
Phaeo.	0.423	0.061	0.183	-0.445	0.592*	1											
NO ₃ -N	-0.531	-0.802***	-0.760**	0.196	0.305	-0.159	1										
NO ₂ -N	-0.583*	-0.575*	-0.503	0.079	0.215	-0.053	0.849***	1									
PO ₄ -P	-0.608*	-0.735**	-0.738**	-0.01	0.49	-0.081	0.727*	0.505	1								
POC	-0.421	0.118	-0.543*	0.371	-0.151	-0.372	0.182	0.227	0.353	1							
TSS	0.234	-0.121	-0.136	-0.432	0.737**	0.815***	0.058	0.125	0.289	0.092	1						
Sand	-0.103	-0.652*	-0.165	-0.471	0.487	0.218	0.43	0.26	0.291	-0.453	0.155	1					
Silt	0.087	0.635*	0.165	0.447	-0.47	-0.211	-0.418	-0.234	-0.275	0.464	-0.141	-0.998***	1				
Clay	0.181	0.710**	0.135	0.605*	-0.53	-0.233	-0.468	-0.386	-0.364	0.372	-0.215	-0.944***	0.924***	1			
TOC	-0.406	0.214	-0.061	0.286	0.074	-0.103	-0.131	0.039	0.222	0.415	0.113	-0.563*	0.569*	0.515	1		
TC	-0.316	0.489	0.133	0.376	-0.229	-0.199	-0.357	-0.135	-0.048	0.437	-0.06	-0.720**	0.721**	0.687**	0.936***	1	
TN	-0.303	0.307	0.089	0.013	-0.021	0.279	-0.203	0.150	-0.009	0.441	0.431	-0.300	0.313	0.210	0.543*	0.587*	1.000

Table 4 Correlation coefficient (r values) between physico-chemical parameters at Chapora Bay during study period

* Significance (P<0.05) ** Significance (P<0.01) *** Significance (P<0.001)

	Temp.	pH	Salinity	DO	Chl <i>a</i>	Phaeo.	NO ₃ -N	NO ₂ -N	PO ₄ -P	POC	TSS	Sand	Silt	Clay	TOC	TC
Temp.	1															
pH	0.973	1														
Salinity	0.961	0.999*	1													
DO	-0.982	-0.912	-0.891	1												
Chl <i>a</i>	0.728	0.867	0.89	-0.586	1											
Phaeo.	0.588	0.759	0.789	-0.425	0.983	1										
NO ₃ -N	-0.958	-0.998*	-1.000**	0.887	-0.894	-0.795	1									
NO ₂ -N	-0.948	-0.996	-0.999*	0.871	-0.909	-0.815	0.999*	1								
PO ₄ -P	-0.948	-0.996	-0.999*	0.871	-0.909	-0.815	0.999*	1.000***	1							
POC	-0.92	-0.804	-0.775	0.977	-0.401	-0.224	0.77	0.747	0.747	1						
TSS	-0.975	-1.000**	-0.998*	0.915	-0.863	-0.754	0.998*	0.995	0.995	0.809	1					
Sand	-0.863	-0.722	-0.688	0.943	-0.282	-0.098	0.682	0.657	0.657	0.992	0.728	1				
Silt	0.873	0.736	0.703	-0.949	0.301	0.118	-0.697	-0.672	-0.672	-0.994	-0.742	-1.000**	1			
Clay	0.739	0.563	0.523	-0.853	0.076	-0.111	-0.516	-0.486	-0.486	-0.944	-0.57	-0.978	0.974	1		
TOC	0.994	0.942	0.925	-0.997	0.649	0.496	-0.922	-0.908	-0.908	-0.957	-0.945	-0.913	0.921	0.808	1	
TC	0.978	0.903	0.882	-1.000*	0.569	0.406	-0.878	-0.861	-0.861	-0.982	-0.907	-0.949	0.955	0.863	0.995	1

Table 5 Two way ANOVA results (p values) of physic-chemical parameters

* Significance (P<0.05) ** Significance (P<0.01) *** Significance (P<0.001)

Parameters	Seasonal	Site wise	Site*Season
Temperature	0.000	0.076	0.594
pH	0.000	0.122	0.001
Salinity	0.000	0.156	0.541
DO	0.001	0.011	0.718
Chl <i>a</i>	0.994	0.02	0.004
Phaeopigment	0.281	0.000	0.005
NO ₃ -N	0.000	0.04	0.006
NO ₂ -N	0.000	0.227	0.229
PO ₄ -P	0.025	0.463	0.907
POC	0.000	0.000	0.029
TSS	0.000	0.000	0.000
Sand	0.020	0.368	0.0001
Silt	0.029	0.356	0.0001
Clay	0.029	0.592	0.004
TOC	0.081	0.000	0.015
TC	0.336	0.465	0.093
TN	0.929	0.004	0.032

Table 6 PC loadings and scores of water parameters at sampling sites during study period 2013–2014

Variables	PC1	PC2	PC3	Samples	Score1	Score2	Score3
Temperature	0.314	0.291	0.107	CB PreM1	0.812	0.346	-1.750
pH	0.176	0.440	0.246	CB PreM2	1.150	1.540	0.529
Salinity	0.331	0.310	-0.206	NC PreM1	0.618	0.401	-2.010
DO	-0.211	-0.068	0.839	NC PreM2	2.120	-0.091	-0.322
Chl <i>a</i>	-0.139	0.451	-0.131	ChB PreM	2.020	-0.487	0.866
Phaeopigment	-0.260	0.422	0.023	CB Mon	-5.540	2.500	0.269
NO ₃ -N	-0.372	-0.227	0.031	NC Mon	-1.660	-1.320	0.178
NO ₂ -N	-0.359	0.033	-0.201	ChB Mon	-2.760	-4.140	-0.017
PO ₄ -P	-0.380	-0.038	-0.340	CB PostM	-0.026	1.750	0.561
POC	-0.337	0.281	0.030	NC PostM	1.680	-0.088	0.628
SS	-0.323	0.326	0.071	ChB PostM	1.580	-0.423	1.060
Eigenvalues	5.73	3.13	1.02				
% Variation	52.1	28.5	9.2				
Cumulative %	52.1	80.6	89.8				

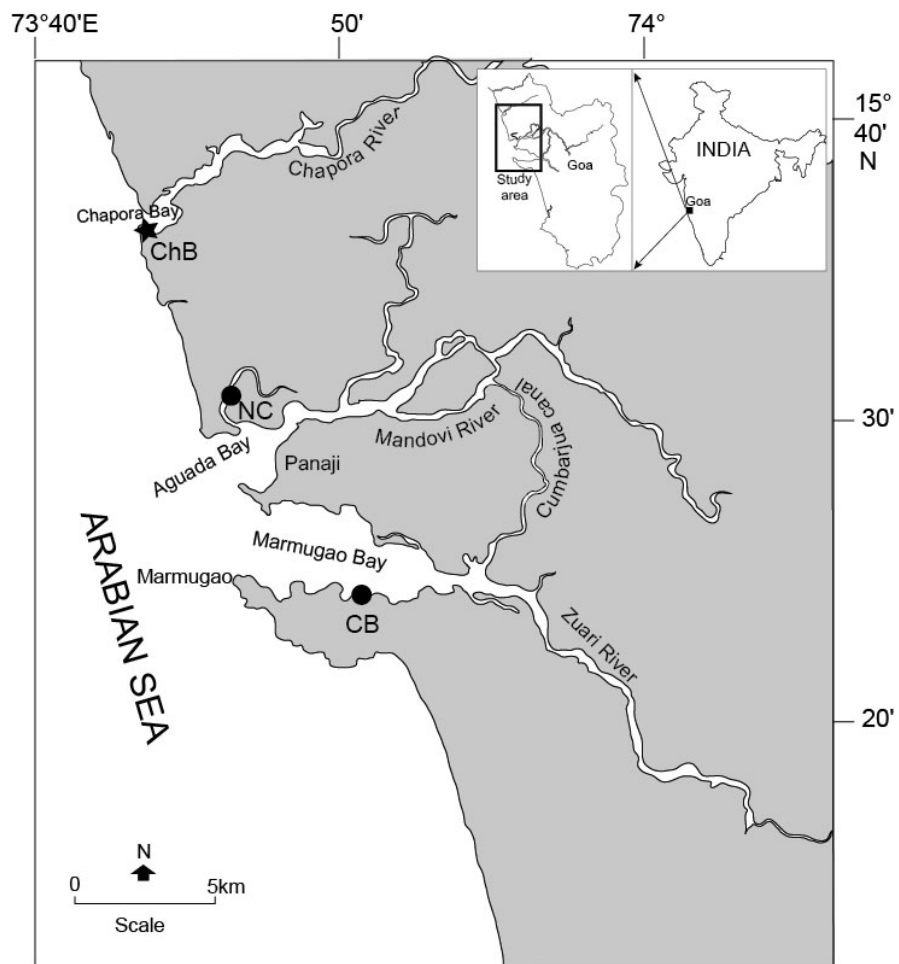


Fig. 1 Map showing sampling sites (CB: Chicalim Bay in Zuari estuary, NC: Nerul Creek in Mandovi estuary, ChB: Chapora Bay in Chapora estuary) along the Goa coast (● : monthly sampling : seasonal★ampling)

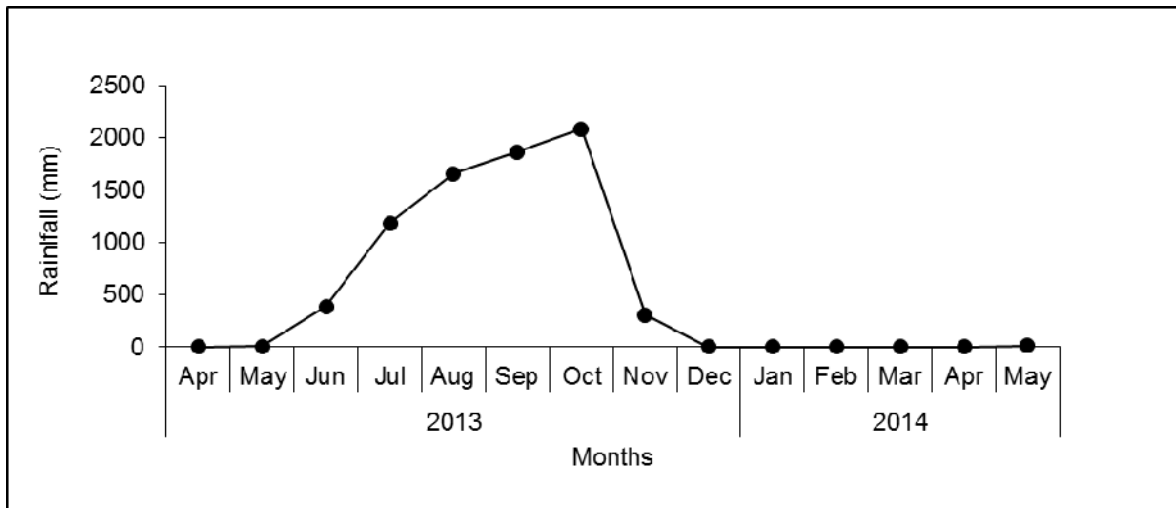


Fig. 2 Monthly variations in rainfall recorded in Goa coast during 2013–2014

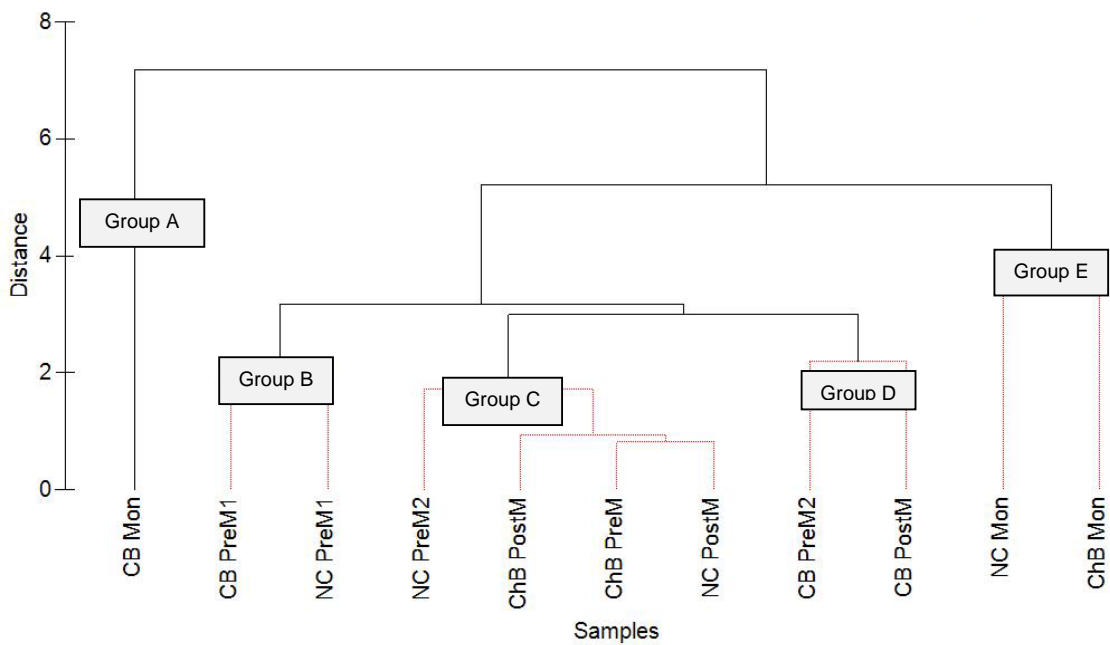


Fig. 3 Dendrogram based on hierarchical clustering method for seasonal variation in water samples at three sites

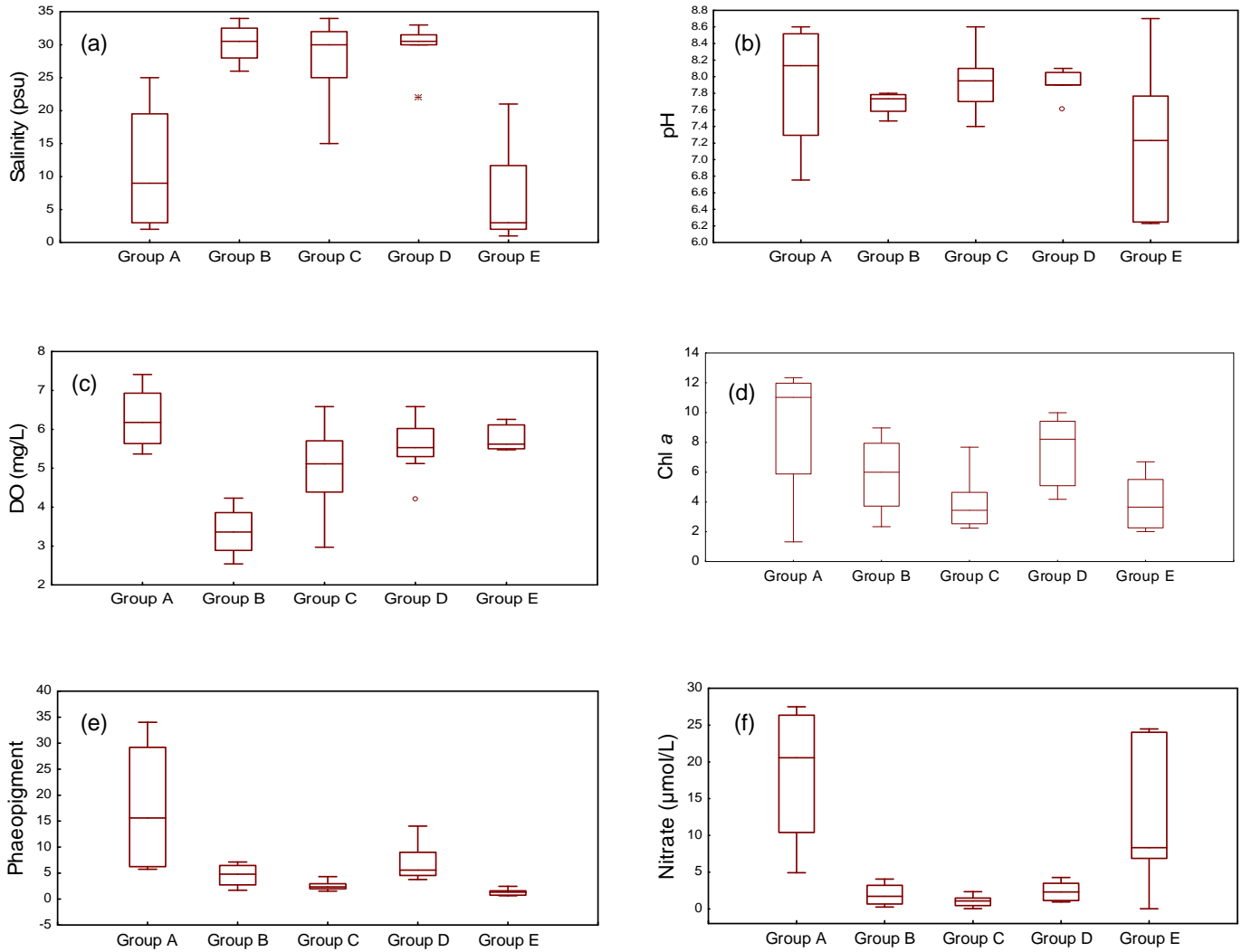


Fig. 4 Box–Whisker–plot for (a) salinity, (b) pH, (c) DO, (d) Chl *a*, (e) phaeopigment, (f) nitrate

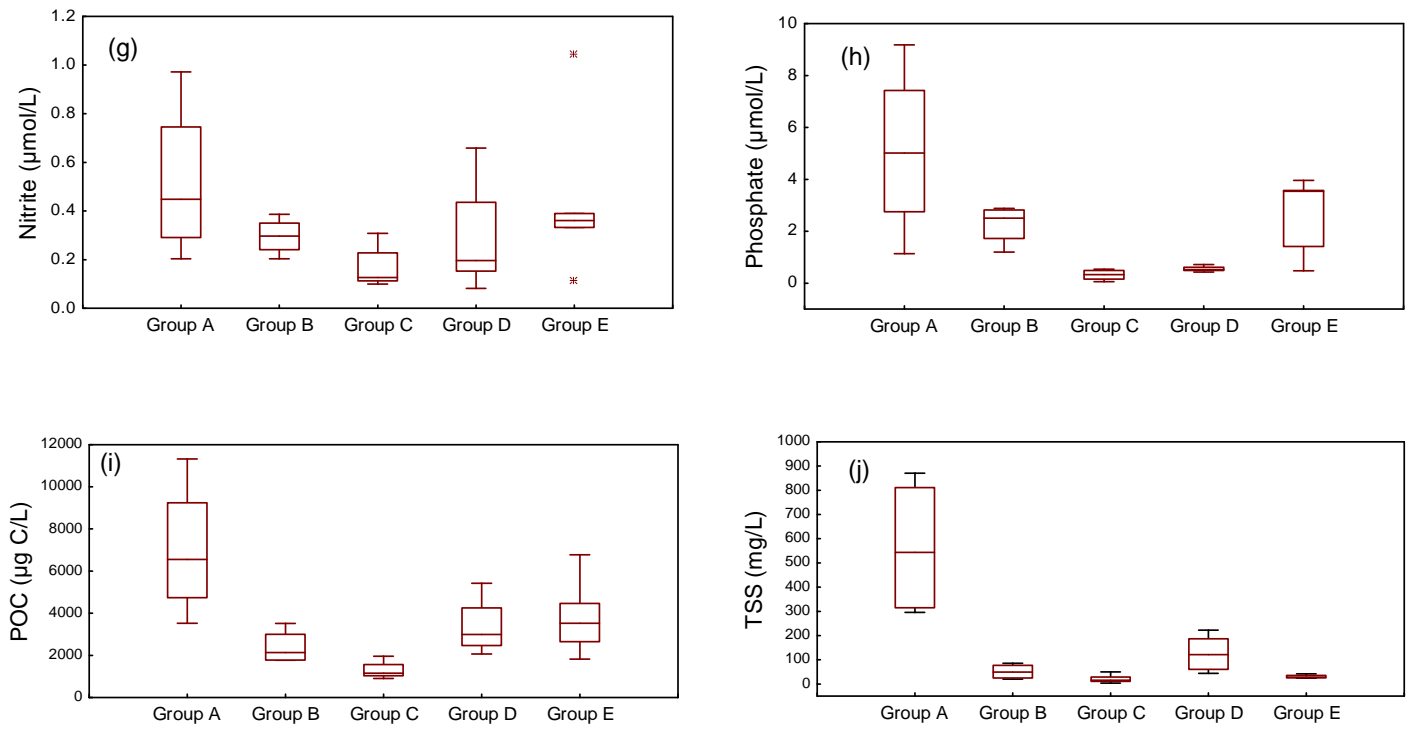


Fig. 4 Box–Whisker–plot for (a) salinity, (b) pH, (c) DO, (d) Chl *a*, (e) phaeopigment, (f) nitrate, (g) nitrite, (h) phosphate, (i) POC, and (j) TSS in five groups