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Diurnal and inter-seasonal variation of nutrients in Dhamra estuary, East coast of India: Application of multivariate Statistical techniques

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Abstract : The research article has focused on intra and inter-seasonal variation of water quality over diurnal and tidal rhythm. Two different seasons were considering for the following study, one from dry period as pre-monsoon and another from the wet period as postmonsoon during the year 2016. The hydro-chemical environmental variables were monitored for 15 variables viz., salinity, pH, water temperature, conductivity, dissolved oxygen, biochemical oxygen demand, suspended solid, nitrite, nitrate, total nitrogen, inorganic phosphate, total phosphate, and silicate. Multivariate statistical analysis was adopted to the data set through person correlation matrix, multi-dimensional scaling, principal component analysis and euclidean distance cluster analysis to know the loading and possible sources of nutrients input to the estuarine water column. The proposed statistical model based on PCA gave a reasonable explanation on the relation between physico-chemical parameters. The PCA extracted five factors in which the first factor attributed to influx of marine water and all the other factors (PC-2 to PC-5) attributed to river run-off during pre-monsoon or dry season. During post-monsoon season or wet period, PCA extracted 4 factors. The first two factors (PC-1 and PC-2) explained positive loading of nutrients attributed to influx of anthropogenic input. It clearly explains nutrients input through riverine system played an active role during post-monsoon or wet season. The PCA-3 and PCA-4 constitute showed less input of nutrients to the estuary. The MDS plot and euclidean distance cluster extracted 3 groups both in dry and wet season by combining 15 environmental variables. All the inorganic-nutrients were clustered in one group while other variables were making a different grouping. This may prove the nutrients are correlated with each other and their sources might be from a common origin of influents and accumulates through riverine discharge.

Keywords : Inter seasonal and diurnal variation, nutrients, Dhamra estuary, East coast of India.

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Introduction

Estuaries are major nutrient suppliers to coastal oceans, breeding grounds for marine organisms, a nursery for juveniles and a potential fishery habitat. Water quality of many estuaries around the world has polluted and degraded due to anthropogenically active nutrient inputs ¹. The water quality of an estuary is influenced by both natural and manmade activities ^{2,3}. The natural processes viz.tidal cycle, precipitation, weathering and soil erosion. Tidal activities play a basic role in the change of physical and chemical properties of coastal water. Manmade activities like industrial and agricultural activities and human exploitation of water resources. The main sources of organic water pollution are domestic and industrial sewage and animal husbandry⁴. Rivers and their tributaries receive many contaminants released from industrial, domestic, sewage and agricultural effluents and finally enter to the marine ecosystem which severely affects the water quality $\frac{1}{2}$ Estuaries are the main entry for nutrients coming from continental drainage to the marine environment⁷. Dissolved nutrients distribution may vary depending on rainfall, fresh water inflow, tidal incursion and also biological activities. The river water provides high levels of nutrients to the water column which make the estuary more productive for natural habitats⁸. Though the nutrients are the basic need for marine biota still its high concentration in estuarine and coastal waters causes several environmental modifications. Unusual supply of nutrients to the coastal body may destroy the ecological balance by eutrophication⁴. Therefore, quantitative and qualitative coastal monitoring and assessment is very much essential of nutrients inputs to ecological system.

Water quality monitoring is essential to control physical, chemical and biological characteristics of water bodies and helps pollution detection. Especially, estuarine water body are facing more risk to contaminants through riverine system. From this point of view, water quality monitoring in many estuaries around the world has been under taken since more than three decades. Since 1990s, extensive monitoring of the coastal waters along the Indian coast has been undertaken by the Ministry of Earth Sciences (MoES). CSIR-Institute of minerals and materials technology, Odisha also took an active part for monitoring of coastal water along Odisha and West-Bengal coast, East coast of India since 1992. Though, we were creating a huge data set, but in this chapter we are only concerning inter seasonal and diurnal changes in the water quality of Dhamra estuary. The Dhamra estuary is a tropical estuary on the East coast of India, and its hydrological characteristics are governed by monsoon regime ⁹. The estuary is a joint stream formed by the convergence of the two rivers i.e. Brahmani and Baitarani located at the south of the town of Chandabali. Brahmani and Baitarani rivers combine together to form Dhamra River before meeting the Bay of Bengal. It is situated on the East coast of India within $86^{\circ}57'$ 00"E - $87^{\circ}01'$ 00" E and $20^{\circ}45'$ 00" N - $20^{\circ}48'$ 00" N. The location of Dhamra Estuary is near proximity to the mineral belt of Orissa, Jharkhand and West Bengal. Dhamra River receives indiscriminate waste discharges mostly agricultural runoff and domestic effluents from two major rivers such as Brahmani and Baitarani. Brahmani River receives effluents from most of the major industries of Rourkela, Angul and Talcher industrial areas of the Odisha state, as a result, the aquatic ecosystem could be exposed to risk¹⁰. Dhamra port, the newly constructed port located northern side of the river mouth which is a source of anthropogenic disturbance on the estuarine water quality as well as ecosystem habitat¹¹. The estuary enclosed with Bhitarkanika mangrove forest and Gahirmatha marine sanctuary. Bhitarkanika wildlife sanctuary famous for its estuarine crocodiles and Gahirmatha marine sanctuary, which is the world's most important nesting beach for Olive Ridley sea turtles on the Orissa coast of Bay of Bengal¹². Both are of international repute being on environmentally sensitive area¹³.



Figure.1. Map of study area

Materials and Methods

The monitoring was carried out from an estuarine point of Dharma river, East coast of India having $20^{0}46'37.35$ "N latitude and 86'057'25.41"E longitude. Diurnal surface water samples were collected in an every tide (LT, MT and HT) for a period of 36 hr. to know the tidal effect on hydro-chemical parameters. By taking this fundamental idea, we have monitored two different seasons like pre-monsoon as dry season and post-monsoon as wet season during the year 2016 (un available of monsoon data).On board measurement was done for the pH, water temperature, conductivity and salinity using WTW kit (multi 340 i). The collected samples were preserved with maximum priority until it reaches to the laboratory (CSIR-Institute of Minerals and Materials Technology, Govt. of India).Suspended solids concentration (SSC), alkalinity, dissolved oxygen(DO) and bio-chemical oxygen demand(BOD) were measured by the standard methods¹⁴.Samples for BOD were incubated in laboratory for five days at 20^{0} C.Nutrient parameters such as nitrite(NO₂-N), nitrate(NO₃-N), ammonia(NH₄-N), silicate(SiO₄-Si), phosphate(PO₄-P), total nitrogen(TN), and total phosphorus(TP) were analysed by standard photometric method¹⁵ using Varian 50 U.V-visible spectrophotometer. Cellulose nitrate membrane filters (pore size 0.45 µm) were used for the measurement of SSC.

Result and Discussion

Seasonal and diurnal variations of environmental variables

The inter-seasonal and diurnal variability in the physic-chemical properties of Dhamra estuarine were well marked. The seasonal variations of environmental variables during two different seasons are cited in the text (Table 1).During pre-monsoon or dry season; the water temperature varied from 29.70 to 30.90^oC (30.45 ± 0.36) , suspended solids 31.03 to 109.36 (60.10 ± 24.27) mg/l, pH 8.06 to 8.13 (8.09 ± 0.02) , conductance 36.70 to 49.50 (43.17 \pm 4.87)mS/cm, salinity 23.94 to 32.99 (29.11 \pm 3.59)PSU, alkalinity 109.87 to 131.76 (119.21± 6.18)mg/l, dissolved oxygen (DO) 4.72 to 6.18 (5.62±0.43)mg/l, biological oxygen demand (BOD) 1.33 to 3.76 (2.87 \pm 0.73)mg/l, nitrite- NO₂ 0.11 to 1.67 (0.77 \pm 0.49) µmol/l, nitrate- NO₃ 6.89 to 13.80 (9.82 \pm 2.23) μ mol/l, ammonia- NH₄0.11 to 3.06 (0.95 ± 0.83) μ mol/l, total nitrogen-TN 16.27 to 37.72 (28.46± 6.45) µmol/l, inorganic phosphate (IP) 0.47 to 1.21 (0.86±0.23) µmol/l, total phosphorous-TP 0.94 to 1.97 (1.19 ± 0.27) µmol/land silicate- SiO₄ 20.63 to 82.01 (46.87±25.47) µmol/l.During post-monsoon or wet season; the water temperature varied from 24.70 to 26.40° C (25.65±0.49) suspended solids 18.50to 180.51 (62.08 ± 48.50) mg/l, pH 7.98 to 8.30 (8.14± 0.10), conductance 21.70 to 35.80 (30.28± 4.59) mS/cm, salinity 13.10to 22.30 (18.93± 3.07) PSU, alkalinity 94.25 to 107.04 (99.61± 3.61)mg/l, dissolved oxygen (DO) 7.35to 8.70 (7.92±0.43)mg/l, biological oxygen demand (BOD) 1.13to 3.01 (1.90± 0.58)mg/l, nitrite- NO₂ 0.24to 1.53 (0.73 ± 0.46) µmol/l, nitrate- NO₃ 2.82to 15.81 (7.74 \pm 4.05) µmol/l, ammonia- NH₄ 0.09to 0.88 (0.36 \pm 0.23) μ mol/l, total nitrogen-TN 13.58to 25.58 (18.11± 3.92) μ mol/l, inorganic phosphate (IP) 0.13 to 1.08 (0.33±0.26) μmol/l, total phosphorous -TP 0.19 to 1.15 (0.49±0.25) μmol/l and silicate- SiO4 10.51to 81.81 (39.72±25.98) µmol/l.

Table 1. Seasonal variation of environmental variables in Dhamra estual	ry
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Descriptive Statistics												
_	Pre	-monsoor	1 I			Post-monsoon						
Parameter	Ν	Min	Max	Avg.	SD	Min	Max	Avg.	SD			
$WT (^{0}C)$	12	29.70	30.90	30.45	0.36	24.70	26.40	25.65	0.49			
SSC (mg/l)	12	31.03	109.36	60.10	24.27	18.50	180.51	62.08	48.50			
рН	12	8.06	8.13	8.09	0.02	7.98	8.30	8.14	0.10			
Cond' (mS/cm)	12	36.70	49.50	43.17	4.87	21.70	35.80	30.28	4.59			
Salinity (PSU)	12	23.94	32.99	29.11	3.59	13.10	22.30	18.93	3.07			
Alkalinity (ppm)	12	109.87	131.76	119.21	6.18	94.25	107.04	99.61	3.61			
DO (mg/l)	12	4.72	6.18	5.62	0.43	7.35	8.70	7.92	0.43			
BOD (mg/l)	12	1.33	3.76	2.87	0.73	1.13	3.01	1.90	0.58			
NO_2 (µmol/l)	12	0.11	1.67	0.77	0.49	0.24	1.53	0.73	0.46			
NO ₃ (µmol/l)	12	6.89	13.80	9.82	2.23	2.82	15.81	7.74	4.05			
NH ₄ (µmol/l)	12	0.11	3.06	0.95	0.83	0.09	0.88	0.36	0.23			
TN (µmol/l)	12	16.27	37.72	28.46	6.45	13.58	25.58	18.11	3.92			

IP (µmol/l)	12	0.47	1.21	0.86	0.23	0.13	1.08	0.33	0.26		
TP (µmol/l)	12	0.94	1.97	1.19	0.27	0.19	1.15	0.49	0.25		
SiO ₄ (µmol/l)	12	20.63	82.01	46.87	25.47	10.51	81.81	39.72	25.98		
Abbreviation: Min.= Minimum, Max= Maximum, Avg= Average, SD= Standard deviation,											
WT= Water Temperature, SSC= Suspended solid, Cond'=Conductance, Salinity = Salinity,											
Alkalinity = Alkalinity, DO=Dissolve Oxygen, Nitrite =NO ₂ , Nitrate=NO ₃ , Ammonia=NH ₄ ,											
Phosphate=PO ₄ , Total Nitrogen =TN, Total Phosphorus=TP											

Variation of temperature was observed during pre-monsoon to post-monsoon. The water temperature was found to be low in wet period than dry period. This type of seasonal changes of temperature was found in other estuaries of Indian subcontinent^{16, 17}. The lowest pH was recorded in pre-monsoon and the highest value was recorded in post-monsoon. The high conductivity during pre-monsoon season due to less mixing of riverine water input from river. The lowest salinity was found in post-monsoon and high in post-monsoon. DO value was found to be higher in post-monsoon due to be low in pre-monsoon and high in post-monsoon. DO value was found to be higher in post-monsoon due to winter cooling and higher photosynthetic activity. The maximum value of BOD was observed in pre-monsoon period due to the maximum biological affinity at elevated temperature and low in winter and reduced flow of riverine water¹⁸. The seasonal variation of SSC was marked during the study period. Higher values (180.51 mg/l) of suspended particulates were obtained during post monsoon, which indicates the river surface run off.

Nutrients, especially nitrogen and phosphorus, are key indicators of water quality in estuaries. Nitrogen and phosphorus naturally enter estuarine waters when freshwater runoff passes over geologic formations rich in phosphate or nitrate, or when decomposing organic matter and wildlife waste get flushed into rivers and streams. Maximum concentration of nitrate (15.81μ mol/l) was observed in post-monsoon. Despite the fact that, the monsoon effect and river discharge into the Dhamra estuary generally cease by the end of September. The similar type of climate was also seen in Zuari estuary^{19,20}. Hence the loading of nitrate released by the riverine discharge still find in the Dhamra estuarine water. This is the reason that the concentration nitrate was found higher in post-monsoon than pre-monsoon. The loading of nitrate in to various estuaries has been observed by others^{16,17}. The other nutrients like NO₂. NH₄. TN, IP, TP and SiO₄ were found a little higher in pre-monsoon. The phosphorous load was found to be high in pre-monsoon which might be due to decomposing of organic matter. The concentration of ammonia found to be higher both in maximum and average scale. The source of ammonia is definitely being from localised and anthropogenic sources input rather than riverine discharge.

Analysis of environmental variables through multivariate statistics

Multivariate statistical tools are more popular today for explaining a large number of data set. Different statistical techniques, including a cluster analysis (CA), principal component analysis (PCA) and factor analysis (FA) were used for this kind of studies. These soft wares tools are capable of assessing temporal and spatial scale variations in coastal water quality, identify potential sources of water contamination and draw a meaningful conclusion ²¹⁻²⁴. Season-wise multivariate statistical analysis of Dhamra estuarine water quality was performed through the cluster, factor, person's correlation matrix and multidimensional scaling using advance software (IBM SPSS 20 and Primer 6). Cluster analysis in the form of Euclidean distance is used to know similarity with on class and dissimilarity between different classes ²⁵. The estuarine data set were standardization through Z-score transformation to avoid misclassification due to wide variability in the data dimensionality²⁶. The statistical analysis, *viz.* correlation matrix and factor analysis were carried out for 15 environmental parameters. Factor loading was calculated using Eigen value greater than 1 and sorted.

Correlation coefficient (r) matrix

The statistical analyses were well formulated and a showed very good result. Seasonal correlation coefficient (r) matrix among physic-chemical parameters during the study period has been cited (Table.2a and 2b).During pre-monsoon or dry season; salinity, conductance and alkalinity were made a strong positive correlation between them. The environmental variables like conductance and salinity showed negative correlation with nutrients. This reflects the concentration of salinity was being affected by the riverine flow²⁷. The inorganic nutrients were not much more influenced by the suspended particulates with NO₂ showed a negative correlation.

Seasonal Pearson Correlation matrix (r) of hydro chemical parameters during Pre-monsoon															
	WT	SSC	pН	Cond'	Sal	Alkal	DO	BOD	NO ₂	NO ₃	NH4	TN	IP	TP	SiO ₄
WT	1														
SSC	.288	1													
pН	.222	018	1												
Cond'	279	218	.116	1											
Salinity	319	200	.008	.969**	1										
Alkal	140	.136	150	.742**	$.800^{**}$	1									
DO	149	.014	.068	412	516	471	1								
BOD	302	032	286	068	116	239	$.680^{*}$	1							
NO ₂	561	578*	248	.340	.387	.254	231	197	1						
NO ₃	026	.241	250	690*	625*	451	.087	064	.120	1					
NH ₄	017	.227	038	.043	075	049	.548	.215	121	203	1				
TN	.637*	.254	220	329	260	175	173	334	193	.231	.215	1			
IP	.492	162	240	116	153	.051	141	238	.312	.149	046	.365	1		
TP	.264	200	.072	240	307	167	.251	.015	204	223	062	007	.334	1	
SiO ₄	.344	.294	077	945**	884**	600*	.398	.126	453	$.640^{*}$	156	.313	.045	.209	1
** Corr	elation	is sign	ificant	at the 0	.01 leve	el (2 tail	ed)								
*Correl	ation is	s signifi	icant a	t the 0.0	5 level	(2 tailed	1)								

Table.2.a Seasonal Pearson correlation matrix (r) of hydrochemical parameters during pre-monsoon.

The nutrients variables like NO_2 , NO_3 , TP and SiO_4 showed a strong negative correlation with salinity, conductance and pH during post-monsoon. This is due to the high rate of riverine flow even after the monsoon time and which was solely responsible for the decrease of their concentration. Suspended particulate was placed the second most importance factor and this was positively correlated with NO_2 , TN and SiO_4 . This may indicated that the rise in nutrient load in the estuarine water due to riverine influx which carried the inorganic nutrients from the land based areas.

Seas	Seasonal Pearson Correlation matrix (r) of hydro chemical parameters during post-monsoon														
	WT	SSC	pН	Cond'	Sal	Alkal	DO	BOD	NO ₂	NO ₃	NH ₄	TN	IP	ТР	SiO ₄
WT	1														
SSC	677*	1													
pН	.617*	708**	1												
Con	.755**	730**	.868**	1											
d'															
Sal	.744**	736**	.883**	.989**	1										
Alka	.223	046	.037	.357	.373	1									
DO	.221	332	.689*	.416	.432	534	1								
BOD	.007	034	.211	017	.001	740**	.790**	1							
NO_2	489	.640*	788**	743**	782**	340	301	.117	1						
NO_3	729**	.483	693*	862**	876**	494	191	.139	.788**	1					
NH_4	.453	353	.222	.289	.389	.105	.113	.183	375	504	1				
TN	801**	.639*	754**	853**	857**	213	319	092	.719**	.895**	481	1			
IP	322	.274	524	545	555	176	272	185	.731**	.699*	334	.689*	1		
TP	394	.218	639*	650*	680*	200	478	278	.730**	.814**	441	.719**	.881**	1	
SiO ₄	735***	.756**	878**	984**	982**	379	413	.042	.802**	.857**	306	.825**	.546	.657*	1

Table.2.b. Seasonal Pearson Correlation matrix (r) of hydro chemical parameters during post-monsoon.

Principal component analysis (PCA)

Principal component analysis during the dry and wet season was extracted through rotation Varimax method using SPSS 20(Table.3).During pre-monsoon PCA extracted 5 factors (PC-1 to PC-5) with Eigen value

>1, which accounts for 82.72 % of the total variance. Seasonal Eigen value plot was cited in the text (Fig.2a and 2b). From the PCA, the first principal component (PC-1) was accounting 28.82% of the total variance with high positive loading towards conductance, salinity and alkalinity and negative towards NO₃ and SiO₄. This may be due to the intrusion of coastal water in to the estuarine body and this can be possible only during HT. PC-2 constitutes (16.27%) with a positive loading of TN and IP, PC-3 and PC-4 accounts such as 14.15 % and 12.31 % with high positive loading towards NH4 and NO₂ respectively. The PC-5 constitutes 11.16 % of the total variance and positive towards IP and TP. The above results indicate the positive loading of inorganic nutrients in the Dhamra estuarine water come from riverine sources during the dry season.

PCA extracted 4 factors which account 90.93% of the total variance during post-monsoon season. PC-1 accounted 40.05% of the total variance and associated with strong positive loading of SSC, NO₃, NO₂ and SiO₄ and negative loading with pH, salinity and conductance. The negative loading of the above factor is due to the fresh water input in to the estuarine system which resulted in the lower of the variables. The positive loading of nutrients is due to the influx of anthropogenic input. PC-2 explains 24.95 % of the total variance and strong positive loading with all the inorganic nutrients. This explained that nutrients input through riverine system played an active role during post-monsoon or wet season. The PCA-3 and PCA-4 constituted 17.03 % and 8.90 % of the total variance and showed less input of nutrients to the estuary.

Seasonal Rotated Component Matrix											
Pre-monsoo	n					Post-mo	onsoon				
	1	2	3	4	5	1	2	3	4		
WT	172	.841	115	383	.082	787	096	052	.436		
SSC		.365	.153	226	753	.889	043	087	180		
pН	.051	130	201	787	.123	829	421	.267	102		
Cond'	.965	184	062	005	.005	881	425	051	.033		
Salinity	.941	188	168	.082	082	866	450	042	.102		
Alkalinity	.804	.082	152	.131	192	193	275	875	.015		
DO	423	217	.805	101	.168	390	262	.840	131		
BOD	154	399	.726	.071	.016	.061	130	.947	.151		
NO2	.284	303	287	.728	.303	.615	.640	.109	043		
NO3	761	.000	244	.420	283	.618	.657	.234	292		
NH4	.162	.232	.794	.050	142	191	245	.055	.893		
TN	194	.822	030	.165	164	.702	.515	013	340		
IP	036	.625	134	.409	.507	.205	.896	062	138		
TP	171	.236	.148	277	.727	.282	.923	150	170		
SiO4	922	.183	.035	098	091	.883	.434	.069	023		
Eigen	4.323	2.440	2.123	1.848	1.675	6.007	3.742	2.555	1.335		
Value											
% of	28.822	16.270	14.150	12.318	11.163	40.048	24.949	17.033	8.897		
Variance											
Cumulative	28.822	45.092	59.242	71.559	82.723	40.048	64.997	82.030	90.927		
%											
Extraction M	lethod: Pr	rincipal C	omponen	t Analysis	s.						
Rotation Met	thod: Var	imax with	n Kaiser N	Normaliza	tion.						

Table.3. Seasonal rotated component matrix (RCM) with vari factors (Principal component, PCs)



Fig.2.a. Eigen curve extracted from PCA during pre-monsoon



Fig.2.b. Eigen curve extracted from PCA during post-monsoon

Multi-dimensional scaling (MDS)

Seasonal multi- dimensional scaling (MDS) were plotted among 15 environmental variables (Fig.3.a and 3.b) by using Primer 6 software. MDS resulted to know the inter relationship and the sources of origin between variables. The pre-monsoon MDS extracted three groups by combining 15 environmental variables. All the inorganic-nutrients with suspended particulate matter were clustered in one group except NO_2 and NH_4 , and rest variables are placed in other two. This may prove the nutrients are correlated with each other and their sources may be similar. The post-monsoon or during wet period the MDS statistics extracted in to three different groups. At one end, all the nutrients were clustered except NH_4 and the remaining parameters consist of other two groups. The grouping indicates there must be a common origin of influents and accumulates through river discharge.



Figure.3.a MDS plot showing relationship between parameters during pre-monsoon



Fig.3.b. MDS plot showing relationship between parameters during post-monsoon

Cluster analysis

Cluster analysis can be used an important tool for analysing water quality data to understand the relationship among stations and months²⁸. Season wise agglomerative Hierarchial clustering (AHC) was performed for all 15 analytical parameters during the year 2016 (Fig.4a and 4b)using advance version of Primer 6 software. Pre-monsoon consist of 2 major clusters or grouping. 1st cluster consist of all the inorganic nutrients along with suspended particulates (except NO₂). Salinity, pH, conductance and alkalinity made the second group just like MDS. Post-monsoon showed two major clusters. The first cluster the nutrient variables like NO₂, NO₃, TN, IP, TP, and SiO4 (except NH₄) were grouped. The 2nd cluster consists of WT, pH, Salinity, conductance and others.







Fig.4.b. Clustering dendogram showing relationship between parameters during post-monsoon

Conclusion

The present summarises with two basic outputs *viz*. riverine influx and localised anthropogenic discharge. The first factor revealed that Dhamra estuarine water was significantly affected by riverine input through Brahmani and Baitarani River. The second factor extracted; anthropogenic discharge through local activities responsible for its change of water quality. Apart from this; the estuary is encircled with Dhamra port and fishing harbour. This could be the main reason behind for the higher nutrient input during pre-monsoon than post-monsoon which was reflected by our current observation. The physicochemical parameters of Dhamra estuarine system were greatly influenced and fluctuated over the diurnal cycle and tidal rhythm. The current observation reflected between inter and intra seasonal variation of nutrient with in the tropical estuary. The variability of hydro-chemical parameters and their fate for their possible sources were undoubtedly delivered through multivariate statistical analysis.

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