Pollution, 2(4): 411-423, Autumn 2016
DOI: 10.7508/pj.2016.04.004
Print ISSN 2383-451X Online ISSN: 2383-4501
Web Page: https://jpoll.ut.ac.ir, Email: jpoll@ut.ac.ir

Seasonal variability in water chemistry and sediment characteristics of intertidal zone at Karnafully estuary, Bangladesh

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Received: 2 Apr. 2016 Accepted: 26 May 2016

ABSTRACT: The Karnafully is one of the most important rivers due to its profound influence on water chemistry and sediment characteristics. The present study intended to assess the quality of water and sediment from intertidal zone of this river in respect to the pollution index. Seasonal water and sediment samples were collected during four seasons (Monsoon, post-monsoon, winter, and pre-monsoon) of 2014. The result indicates that these investigated parameters ranged as water temperature (21.7-36 °C), pH (8.0-8.7), salinity (2.4-8.8‰), total suspended solid (0.08-0.8 g/L), dissolve oxygen (0.00-4.52 mg/L), soil temperature (21.3-33 °C), pH (5.0-6.8), sand (4.13-44.10%), silt (39.93-75.89%), clay (11.98-21.19%), soil organic matter (4.33-6.21%), organic carbon (2.5-3.6%), nitrite-nitrogen (0.69-3.97 µg/L), and phosphate-phosphorus (0.23-3.44 µg/L). Multivariate statistical analyses like post-hoc LSD test, Cluster Analysis (CA), and Principal Component analysis (PCA) brought out the spatial and temporal changing pattern of water chemistry and sediment characteristics with the effect of uprising pollution. CA ascertained the compatibility among different parameters and categorized the monitoring sites into highly and moderately polluted areas. Moreover, PCA brought out five primary components and highlighted the three dormant factors, enormously regulating the river water chemistry such as municipal waste, carbon based nitrogenous compound, and local geomorphological weathering process. This investigation provided an outline on deterioration of water and sediment quality by high anthropogenic impact and suggests national policy maker to take some initiatives for retaining the quality water and sediment properties.

Keywords: cluster analysis, intertidal zone, pollution index, principal component analysis, spatio-temporal variation.

INTRODUCTION

Intertidal zone of estuarine system characterized by spatio-temporal variation in seasonal time frame reflects on its hydrological and sedimentological nature. Physico-chemical features of estuaries are not steady-state systems while water chemistry and sediment properties are considered as the controlling factors (Förstner, 2004). Seasonal fluctuation exerts a profound effect on nutrient cycling, sediment dynamics, and coastal

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geomorphology. Sediment acts as the nutrient reservoir in aquatic system that indicates the overlaying water quality (Anilakumary et al., 2007). Rapid urbanization and anthropogenic activities are rapidly degrading the estuarine water quality (Wang et al., 2014; Jiang-Qi et al., 2013). Continuous accumulation of pollutants due to bio-geological mechanism causes the variability in water chemistry and sedimentation pattern (Singare et al., 2011).

Deposits size classes are crucial in evaluating the qualities of sediment dynamic and complex nature of estuary. Wave, tide, current, salinity, precipitation, and diffusion processes can transport the energy of detritus to the water column (Jorcin, 2000). Coastal subsidence, landmass erosion, decomposition process, wind, and water carry sediment to the river. Suspended and dissolved materials deposited on the bottom of the water column and made a reservoir for pollutants and trace elements. Sediment dynamics of intertidal mudflat have an impact on ecological quality (Brils, 2008).

The Karnafully estuary is the most typical estuary where tidal oscillation and fresh water discharges are dominantly acting together in creating high mixing mechanism (Mahmood et al., 1976). Thousands of industries and factories are situated on the bank of the Karnafully and do not have any effluent treatment facilities (Das et al., 2002). So, untreated industrial waste is mixed with adjacent coastal water and finally drains to the Karnafully through different canal systems (Sarwar et al., 2010). Industrial waste contains lots of toxic substances that, directly or indirectly, affect aquatic ecosystem (Ahmed, 2000). Therefore, systematic and appropriate monitoring of the status of pollution level is needed.

Researchers have studied the surface water chemistry, sedimentological characteristics, and seasonal fluctuation (Ajayan and Kumar, 2016; Damotharan et al., 2010; Prasanna and Ranjan, 2010; Pradhan et al., 2009; Srivastava et al., 2009; Prabu et al., 2008; Raja et al., 2008; Mahmood et al., 1976). Water and sediment features in coast are rapidly changing with time and space, so regular monitoring is needed to retain their quality (Satheeshkumar and Khan, 2012). The present study is very effective to enrich our knowledge about the nature and effect of pollution on this dynamic estuary. The present baseline information water quality parameters and sediment characteristics would form a useful tool for further ecological assessment and monitoring the quality of water and sediment.

MATERIALS AND METHODS

Study area

Sediment and water samples were collected from intertidal zone of Karnafully estuary, situated at Chittagong coast adjacent to the Bay of Bengal. The area of study is shown in Figure 1. Among these sites, Chaktai canal (Site 1) was envisaged as mostly-impacted location, Govt. Fish landing station (Site 2) was considered as moderately-impacted site and Eastern side of the Karnafully Bridge (Site 3) was selected as less-impacted site according to the hydro-morphological characteristics as well as pollutant load.

Sample analysis

Temperature, pH, and total suspended solids were measured by standard methods (APHA, 2005). Soil organic carbon (SOC) was measured by Walkey and Black wet oxidation method modified by Huq and Alam (2005). Soil organic matter was measured following Parsons et al. (1979). Soil texture (% of sand, silt, and clay) was analyzed by the hydrometer method following Bouyoucos (1962) modified by Huq and Alam (2005).

Statistical methods

Statistical methods on dataset depicted One-way ANOVA (Post-hoc LSD test) with multivariate statistical methods such as PCA and CA. In present study, one-way analysis of variance (Post-hoc LSD) at 95%

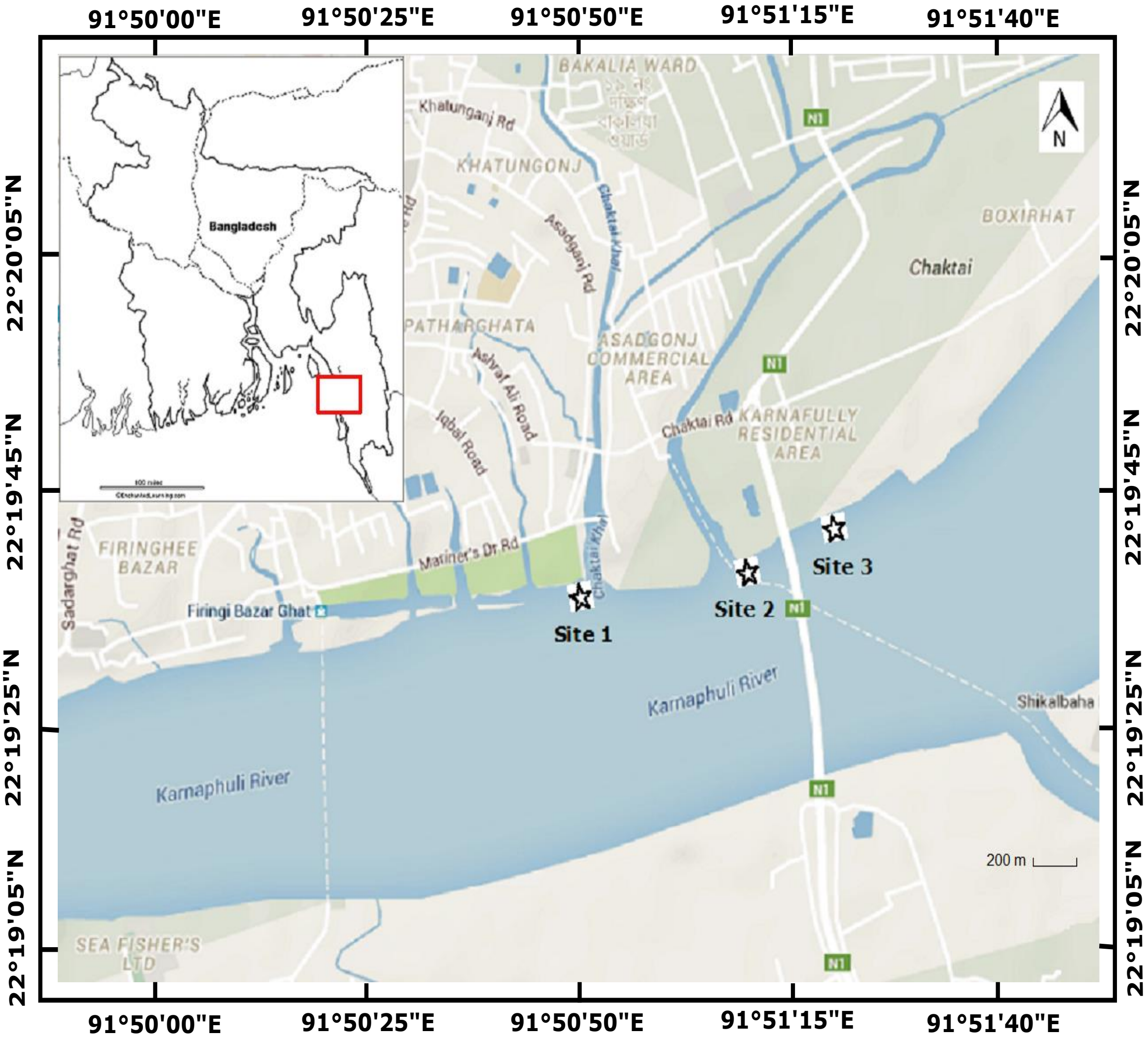

Fig. 1. Location of water and sediment quality monitoring sites in the Karnafully Estuary

of confidence level was applied to find out the significant spatial and temporal variations of water and sediment quality parameters. CA is an effective tool for characterization and simplification of data sets with the behavior they possess. It is also a very effective tool to sort out the similarity and dissimilarity with the influencing factors on different datasets (Wang et al., 2014). PCA was applied to find out the principle factors of variation in dataset with simplification and classification of raw data. It also provides guidelines on spatial and temporal distribution of resultant factors (Singh et al., 2004). Five principal components were expressed which contain the eigenvalue more than 1 (Gupta et al., 2008). All of the analysis was performed using PASW statistics 18, Microsoft office 2007, and MINITAB-14.

RESULTS AND DISCUSSION

Spatial and temporal variability in water quality parameters

Hydrological quality of the studied sites varied from season to season as well as from location to location. One-way ANOVA (Post-hoc LSD) test showed the significant spatial and temporal variation of different water quality parameters. Water temperature was kept at the highest value (36°C) throughout monsoon at site 3 and the lowest value (21.7°C) noted from site 1 in winter (Figs 2 & 3). At the time of monsoon (post-monsoon: P=0.00; winter: P=0.00) and pre-monsoon (post-monsoon: P=0.01; winter: P=0.00), mean water temperature was found significantly higher than post-monsoon and winter (Fig. 3). Maximum water pH (8.7) was found at site 3 in monsoon and pre-monsoon, whereas minimum (8.20) was investigated from each site during every season except monsoon (Figs. 2 & 3).

In addition, water salinity (8.84‰) was peaked at site 1 throughout winter and the lowest value (2.43‰) was observed from the same site in monsoon (Figs. 2 and 3). Mean water salinity resembled significantly higher in winter than monsoon (P=0.00), post-monsoon (P=0.00), and pre-monsoon (P=0.00) and there is no significant difference between post-monsoon and pre-monsoon. A consecutive changing trend on salinity noted from monsoon to pre-monsoon and descending from one another as: winter > post-monsoon > pre-monsoon > monsoon (Fig. 3).

The highest total suspended solid was investigated (0.80g/L) at site 3 all over the pre-monsoon period, whereas the lowest (0.08 g/L) was recorded from site 3 in monsoon. In contrast, maximum dissolved oxygen (4.52 mg/L) was recorded at site 3 throughout post-monsoon and minimum was found during winter at site 2 (Figs. 2 & 3). Mean dissolved oxygen (DO) was found significantly lower in site 2 (Site 1: P=0.00; site 3: P=0.00) rather than site 1 and site 3 (Fig. 2). Rest of the parameters, like water temperature, water pH, and total suspended solid, (TSS) represented non-significant variation among the sampling sites. Throughout the four seasons, mean water pH, total suspended solid (TSS), and dissolved oxygen (DO) were remained almost in uniform trend with non-significant variation.

Spatial and temporal changes in sediment quality parameters

Maximum soil temperature (33.0°C) was inspected from site 2 and 3 in pre-monsoon and minimum (21.3°C) noted from these two sites during winter (Figs. 2 & 3). Mean soil temperature during monsoon was found significantly higher than post-monsoon (P=0.00) and winter (P=0.00) but significantly lower than pre-monsoon (P=0.00). Soil temperature sequentially changed from pre-monsoon to winter and significantly descended from one to the other as: pre-monsoon > monsoon > post-monsoon > winter (Fig. 3). On the other hand, maximum soil pH (6.8) was recorded from site 2 in pre-monsoon and minimum (5.0) noted in site 1 throughout post-monsoon (Figs. 2 & 3). Mean soil pH in site 1 (site 2: P=0.03; site 3: P=0.011) was remained significantly lower than sites 2 and 3 (Fig. 2). Among the sediment texture classes, highest percentage of sand (44.03%) was recorded during monsoon from site 1 and lowest (8.13%) was reported at site 3 during post-monsoon. Percentage of silt (75.89%) peaked at site 3 during monsoon and the lowest (39.93%) value was also recorded from the same sampling site during pre-monsoon (Figs. 2 & 3). Mean concentration of silt in site 3 (P=0.04) was observed significantly higher than site 2 (Fig. 2).

Soil organic matter content was noted the highest (6.21%) at site 2 in winter and the lowest content (3.72%) was recorded from site 3 during post-monsoon (Figs. 2 & 3). Mean soil organic matter (SOM) was found significantly higher in site 2 in comparison with site 1 (P=0.00) and site 2 (P=0.00), but there is no significant variation between site 1 and site 3 (Fig. 2). Soil organic carbon was also investigated highest (3.74%) at site 2 during pre-monsoon and the lowest content (2.06%) was reported at site 3 during monsoon (Figs. 2 & 3). Mean SOC in site 2 remains significantly higher than site 1 (P=0.00) and site 2 (P=0.00) (Fig. 2) but the rest of the soil quality parameters, such as soil temperature (STem), soil NO_2-N, soil PO_4-P, % of sand, and clay do not show any significant spatial variation.

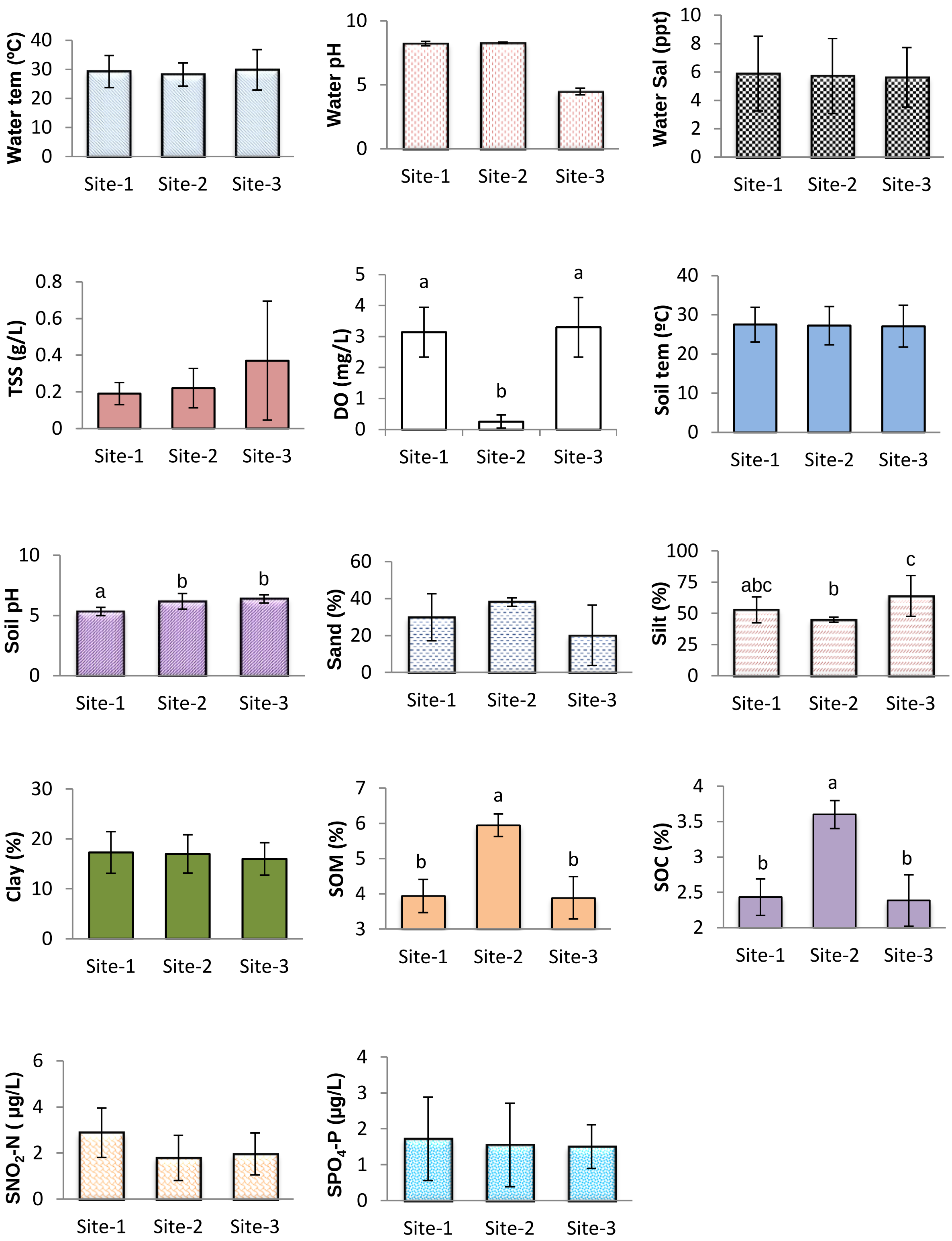

Fig. 2. Spatial variation (Mean±SD) of water and sediment quality parameters. Bars with the same letter are statistically indifferent.

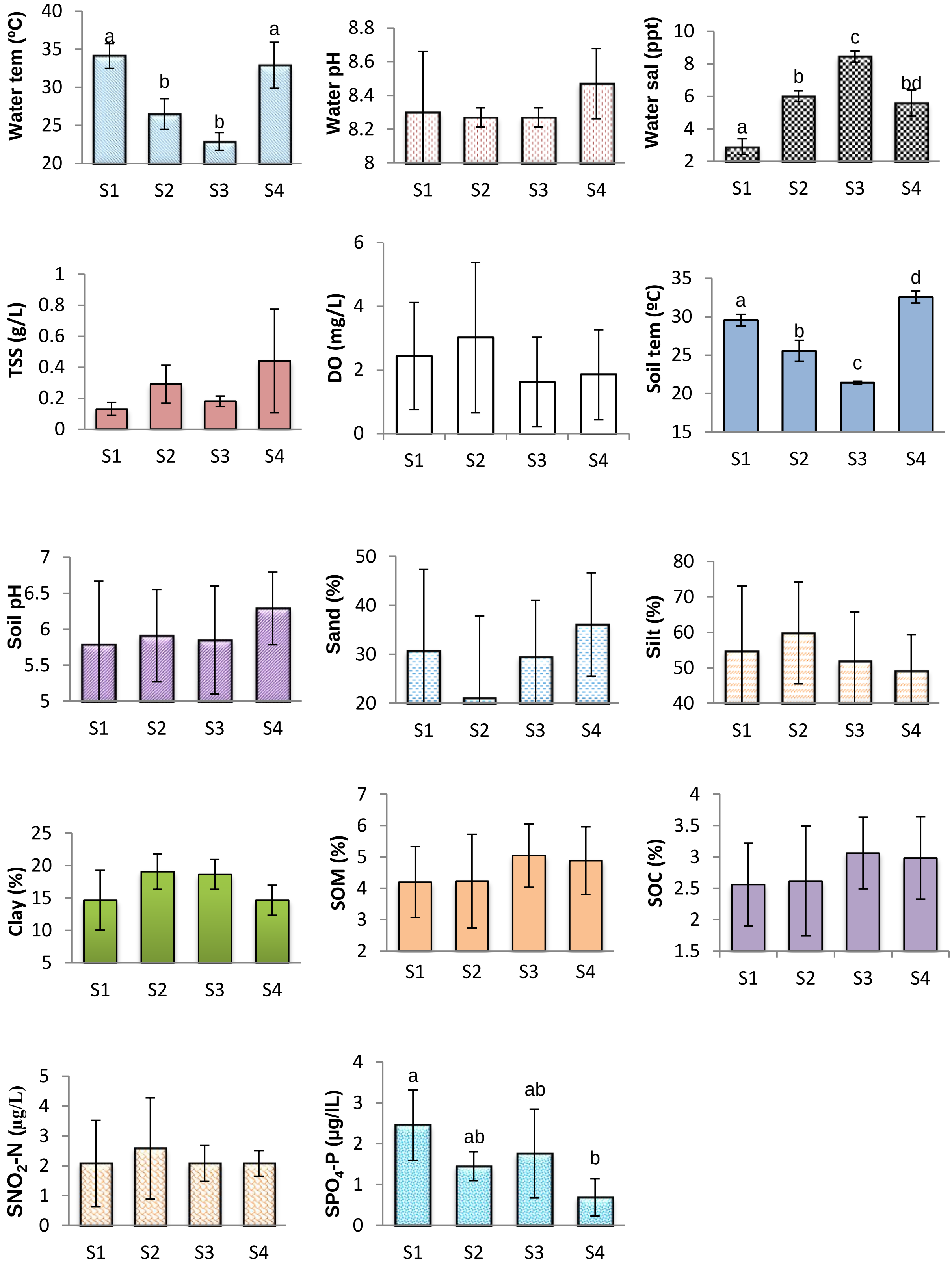

Fig. 3. Temporal variation (Mean±SD) of water and sediment parameters. Bars with the same letter are statistically indifferent. (S1= monsoon; S2= post-monsoon; S3= winter and S4= pre-monsoon)

Maximum soil PO_4-P was found (3.44 µg/L) during monsoon at site 1 and minimum (0.23 µg/L) was investigated from site 2 in pre-monsoon. Peak NO_2-N (3.57 µg/L) was recorded from site 1 and the lowest (0.69 µg/L) was investigated from site 3 throughout post-monsoon (Figs. 2 & 3). Mean soil PO_4-P was investigated significantly higher during monsoon (P=0.02) than pre-monsoon, whereas non-significant variation was found in comparison with rest of the two seasons. Without these parameters, rest of the soil quality parameters, like SpH, SOM, SOC sand, silt, clay, and soil NO_2-N, do not show any significant temporal variation (Fig. 3).

In Coastal areas of Bangladesh, temperature varies between 25-30°C with noticeable seasonal fluctuation. Temperature values were significantly higher in the monsoon months and lower in winter months due to local climate condition which is mainly inclined by the southeastern and northwestern wind pattern prevailing in the Bay of Bengal (Holmgren, 1994). A similar trend was described in previous studies (Chowdhury et al., 2010; Kamal et al., 2009). Optimal pH range for sustainable aquatic life is pH 6.5-8.2 (Murdoch et al., 2001). Anything either highly acidic or alkaline would kill marine life. The water pH remains alkaline throughout the study period at all sampling sites. The high pH observed during monsoon season at site 3 may be due to the influence of fresh water influx, dilution of sea water, low temperature, and organic matter decomposition.

Minimum TSS recorded during monsoon may be caused by receiving huge amount of crystal clear water from hilly area in this season while maximum value was recorded in pre-monsoon for high mixing process caused by tornado, typhoon, cyclone, and other natural process in this season. Concentration of DO implied that sampling site 2 is the highly polluted area and it is difficult to sustain for aquatic organisms. Furthermore, site 2 is the main discharge point of Chittagong city and continuously discharging huge amount of domestic and industrial waste. Insufficient dissolve oxygen in the water column causes the anaerobic decomposition of organic matter which tends to cause the formation of noxious gases such as hydrogen sulphide and development of CO_2 and methane in the intertidal and coastal bottom sediment layer (Ravaniah et al., 2010).

Sediments of the intertidal zone of Karnafully estuary resembled almost neutral to slightly acidic. Gradual decrement of soil pH will enhance the metal toxicity and adverse effect on aquatic organisms (Singare et al., 2011). Present study snapped out that silt was dominant in sediment texture. Therefore, water holding capacity, cation exchange capacity, pH buffering capacity, and organic matter were remained low. High siltation rate was found in monsoon for strong wave action, high turbulence, and high terrestrial runoff. Redox potential is low in soil with fine grained deposits characteristics (Kunickis et al., 2010). SOM levels in all mineral soils commonly range from 4-7% of the total soil mass (Wagai et al., 2009). Higher value of organic matter found in winter and post-monsoon period may be due to large amount of humus transported by the rivers and dominancy of mud in sediment during these seasons (Manjappa et al., 2003).

Nitrates are the most oxidized form of nitrogen and also play a vital nutrient for growth, reproduction, and the survival of aquatic organisms. Excess concentration in nitrate level (>1 mg/L) is not good for aquatic life (Adeyemo et al., 2008). The higher nitrate value was investigated during monsoon and post-monsoon at site 1 due to the presence of organic material. Nitrate level increasing in monsoon and subsequent season was due to the rainfall, freshwater inflow, decomposition processes (Prabu et al., 2008). Another possible way of nitrates entry is through oxidation of ammonia from nitrogen to nitrate formation (Rajasegar, 2003). Lowest value was recorded from site 3 during post-monsoon due to the absence of terrestrial discharge, photosynthetic activity, and water dominancy.

Phosphates are very essential nutrients that play a vital role on the growth of organisms and limit the primary productivity of aquatic environment. Inorganic phosphorous plays a dynamic role in aquatic ecosystem when present in low concentration, but high concentration of phosphate causes eutrophication (Manikannan et al., 2011). Highest value obtained from monsoon at the site 1 was due to freshwater circulation and mixing processes. Another cause of increasing PO_4-P in this season may be due to regeneration and release of total phosphorus from bottom mud into the water column by turbulence mechanisms (Saravanakumar et al., 2008). Lowest value obtained from pre-monsoon at site 2 may be attributed to limited flow of freshwater, low precipitation, salinity intrusion, and utilization of phosphate by phytoplankton.

Cluster analysis

Multivariate statistical analysis, such as Cluster Analysis (CA), Principal Component Analysis (PCA), and Factors Analysis (FA) act as an effective index for meaningful interpretation of spatio-temporal parametric data. Many researchers have used these techniques to assess and characterize the water quality. Wang et al. (2014) used these statistical analyses to evaluate the variance of water chemistry. Moreover, Talukder et al. (2016), Wang et al. (2012), Jiang-Qi et al. (2013), Venkatesharaju et al. (2010), Qadir et al. (2007), and Kowalkowski et al. (2006) demonstrated that multivariate statistical methods (PCA, CA, FA) can be very effective to interpret the complex data sets, identify pollution factors, and assess water quality with spatio-temporal deviation.

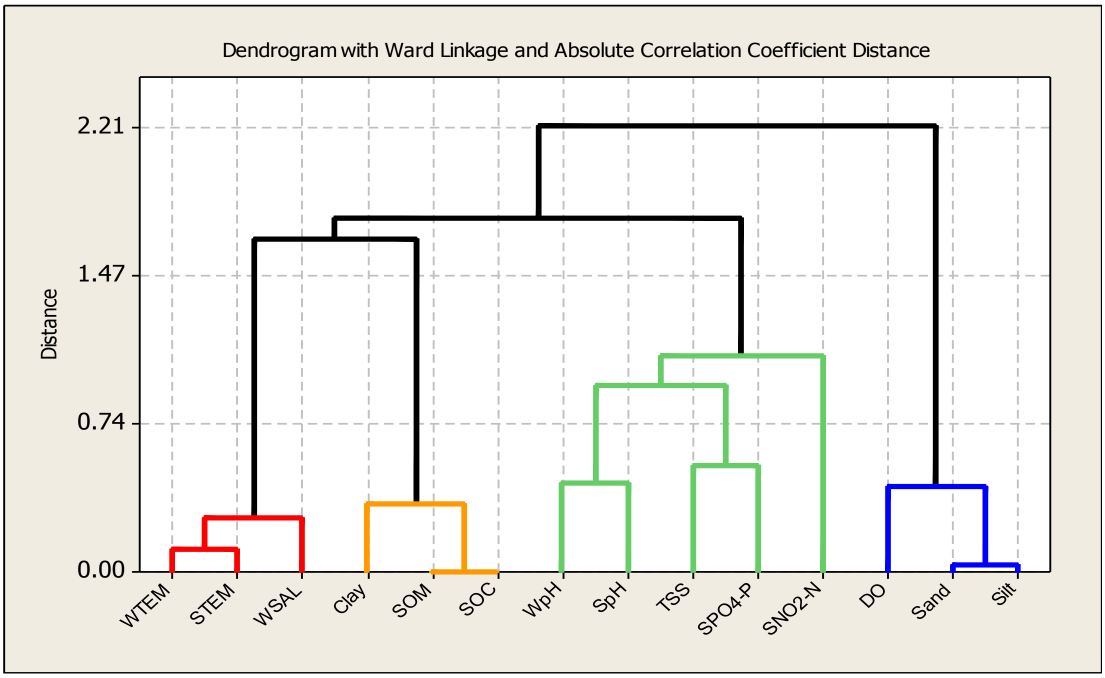

Fig. 4. Dendrogram of water and sediment quality parameters (Four colors are representing four clusters; WTEM= Water temperature; STEM= Soil temperature; WSAL= Water salinity; SOM= Soil organic matter; SOC= Soil organic carbon; WpH= Water pH; SpH= Soil pH; TSS= Total suspended solid; SPO_4-P= Soil phosphate-phosphorus; SNO_2-N= Soil nitrite-nitrogen; DO= Dissolve oxygen)

Amalgamation steps of cluster analysis (CA) were performed using ward linkage with absolute correlation coefficient distance. Firstly, CA was applied among the water and sediment quality parameters, which brought out four significant clusters: cluster 1: WTEM, WSAL; cluster 2: WpH, TSS, SpH, SNO_2-N, SPO_4-P; cluster 3: DO, Sand, Silt; and cluster 4: Clay, SOM, SOC (Figure 4). Parameters clustered in minimum distance have a high affinity with the same identical behavior during seasonal changes and also have a potential influence on each other. WTEM, STEM, and WSAL render a linkage in minimum correlation coefficient distance and demonstrate the obsessing power during seasonal changes. Cluster 4 indicates that SOM and SOC in sediment largely governed by clay content during seasonal changes, likely WpH, SpH; SNO_2-N, SPO_4-P; sand-silt represents minimum cluster distances as well as strong relevance in environmental process.

Secondly, CA was applied among the sampling sites to find out the spatial similarity of water and sediment quality parameters. The CA results rendered a dendrogram, where three sampling sites were classified into two clusters: Cluster 1: site 1 and site 2; Cluster 2: site 3 (Fig. 5). The sampling site in each cluster has an almost homologues trend of water and sediment quality variability with similar water pollution types and strengths. Site 1 and site 2 are clustered in minimum correlation co-efficient distance and yield the higher level of pollution on sediment and water column. Site 2 is situated in the mouth of the Chaktai canal, which is the main discharge point of the Chittagong city and is highly affected by untreated industrial effluents and domestic wastes. Site 3 is situated far from the direct discharge point but influenced by untreated industrial and domestic wastes, so it can be considered as moderately-polluted area.

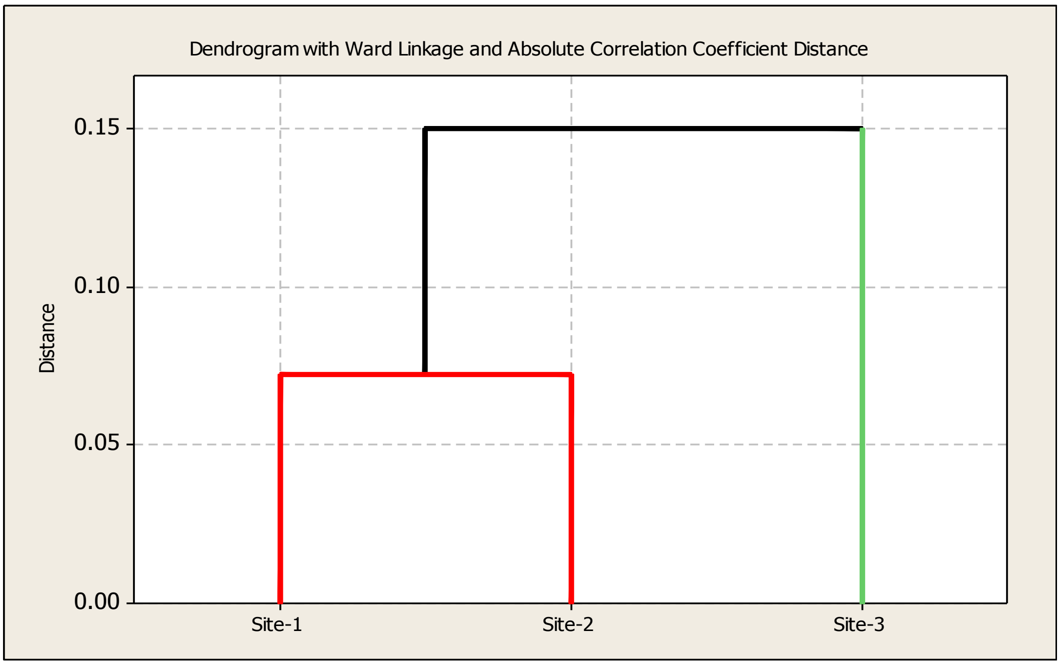

Fig. 5. Dendrogram of sampling sites in accordance with water and sediment quality parameters from intertidal zone of Karnafully river estuary (Two different colors are representing two different clusters).

Principal component analysis

Principal component explained the most important factors affecting the water and sediment quality of the study area. PCA results are listed in Table 1, including rotated loading, percentage of each major factor, and initial eigenvalues. PCA-1 had a highest initial eigenvalue 3.97 and explained 28.35% of total variance, with strong positive loading of SOM, SOC. Clay particle, moderate positive loading of TSS, and moderate negative loading of SpH resembled the loading of pollution mainly caused by untreated organic load with crucial anthropogenic effect. PCA-2 comprised with the eigenvalue 2.72 and explained 19.43% of total variance, with strong positive loading of WTem and Stem. High negative loading of WSal can be represented as effective geological changes on environmental parameters. PCA-3 explained 17.19 percent of total variance, with strong positive loading of DO and silt. Strong negative loading of sand represented the huge loading of municipal waste and land-based washed materials. PCA-4 explained 14.24 percent of total variance moderate positive loading of WpH, SpH, TSS; moderate negative loading of SPO_4-P, which is an indication of inorganic load on the water column and sediment of the study area. PCA-5 explained 7.48% of total variance with strong positive loading of SNO_2-N, which is also a signal of carbon-based nitrogen contamination in sediment.

Table 1. Rotated component loadings of the three principal components including eigenvalue greater than one, percentage of total variance, cumulative percentage

Variable	PCA 1	PCA 2	PCA 3	PCA 4	PCA 5
WTEM	-0.124	**0.963**	0.018	0.114	0.042
WpH	0.016	0.328	0.242	**0.750**	-0.031
WSAL	0.106	**-0.918**	0.007	0.231	0.040
TSS	**0.544**	0.251	-0.198	**0.608**	0.008
DO	0.244	0.163	**0.801**	-0.145	0.293
STEM	-0.173	**0.853**	-0.172	0.326	0.078
SpH	-0.484	-0.012	0.122	**0.713**	-0.143
Sand	-0.025	0.183	**-0.964**	-0.038	0.113
Silt	-0.176	-0.067	**0.967**	0.104	-0.052
Clay	**0.762**	**-0.455**	0.072	-0.246	-0.241
SOM	**0.954**	-0.130	0.030	0.064	0.027
SOC	**0.955**	-0.130	0.029	0.065	0.031
SNO_2-N	-0.033	0.033	0.025	-0.077	**0.973**
SPO_4-P	-0.108	0.142	0.134	-0.783	0.007
Eigenvalue	3.094	2.994	2.674	2.334	1.140
% of total variance	22.102	21.385	19.103	16.668	8.143
Cumulative (%)	22.102	43.487	62.590	79.258	87.401

Extraction Method. Principal Component analysis; Rotation method: Varimax with Kaiser Normalization and rotation converged in 6 iterations. Bold data are the main contribution elements to the component.

River pollution Index (RPI)

River pollution index (RPI) is used simultaneously by different organizations such as Taiwan EPA to evaluate the surface water quality. It is a simple method comprising concentration level of four parameters: DO, BOD, SS, and NH_3-N. Four-state of quality is calculated for each parameter to evaluate the pollution status. The RPI is computed using the following equation (Liou et al., 2004):

$$\mathrm{RPI} = 1/4\sum_{i=1}^{4}\mathrm{Si}$$

Table 2. River Pollution Index (RPI) Chart (Chen et al., 2012; Liou et al., 2004)

Items/ ranks	Good	Less polluted	Moderately pol.	Highly polluted
DO (mg/L)	>6.5	4.6-6.5	2.0-4.5	<2.0
BOD_5 (mg/L)	<3.5	3.0-4.9	5.0-15	>15
SS (mg/L)	<2.0	20-49	50-100	>100
NH_3-N (mg/L)	<0.5	0.5-0.9	91.0-3.0	>3.0
Index scores (Si)	1	3	6	10
Sub-index	<2	2.0-3.0	3.1-6.0	>6.0

In present study, concentration of DO and TSS were compared with concentration of RPI table to weigh the status of particular water parameters (Table 2). Average DO in site 1 is 3.1425 mg/L that is a clue of moderate pollution in comparison with RPI. Average DO in site 2 remains 0.1275 mg/L which can be treated as highly polluted area according to RPI. In site 3, average DO was found to be 3.24 mg/L, which renders moderate pollution in this area according to RPI table. Average TSS in every sampling site was found >100 mg/L that is a hint of high pollution according to RPI (Chen et al., 2012).

CONCLUSION

Multivariate statistical methods were successfully used in this study to find out the variability of different sediment and water quality parameters along the intertidal zone of Karnafully river estuary. Post-hoc LSD test found out that parameters like dissolved oxygen, soil pH, silt, sediment organic matter and carbon, water and soil temperature, salinity, and soil PO_4-P were significantly changed spatially and temporally. CA characterized the sampling sites into two categories: highly-polluted and moderately-polluted. CA also found out the inter-parameter relationship during geological process. PCA explained three prominent factors: municipal wastes, carbon-based nitrogen compound, and geological weathering process predominantly affecting the water and sediments of Karnafully river estuary. Site 2 (Mouth of the Chaktai canal) is the one of the major discharge points of the Chittagong city where no DO was found during winter season. It is a clear indication of high organic load. Present study renders that site 1 and site 2 are the highly affected by anthropogenic pollution, so effective initiative should be taken both nationally and internationally to save the river Karnafully.

ACKNOWLEDGEMENTS

The authors are grateful to the Institute of Marine Sciences and Fisheries, University of Chittagong, Bangladesh for laboratory facilities to conduct this research. We are thankful to the Department of Planning and Development, University of Chittagong, Bangladesh for financial support. We are also grateful to honorable reviewers and the editors who have helped to tremendously improve the manuscript.

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