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SEASONAL DYNAMICS OF NUTRIENTS IN THE SEDIMENT OF MANAKUDY ESTUARY, TAMILNADU, SOUTH-WEST COAST OF INDIA

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Abstract: Temporal variations in estuarine systems can have direct and indirect effects on factors influencing fluxes. Nutrient concentrations and distributions have seasonal patterns. A detailed study on the sediment nutrients of Manakudy estuary was undertaken over a period of one year. The present study is mainly focused on the seasonal variation in the concentration of nutrients during pre-monsoon, monsoon and post-monsoon seasons of 2011 – 2012. The investigation included the estimation of pH, Redox potential, Electrical conductivity, Total soluble salt, Organic carbon, Chloride, Total Nitrogen, Phosphate-Phosphorus, Sulphate-sulphur, Calcium, Magnesium, Sodium and Potassium of this estuarine sediments. The sediment pH was noticeably alkaline throughout the study period ranging from 7.48 to 8.3. E*h* varied from -28 mV to -78 mV. Electrical conductivity varied from 0.09 mS/cm to 9.9 mS/cm. The percentage of Total soluble salt was minimum during monsoon season. The concentration of nutrients recorded was minimum during monsoon and maximum during non-monsoon seasons. Further the concentration of nutrients was found to be maximum at station 6 in all the three seasons with a few exceptions only. This indicates that out of the ten stations selected, station 6 was the most polluted station where there is inflow of untreated sewage and inflow of water from agricultural fields. Thus the study clearly shows that the nutrient concentrations are fluctuating from season to season, which implies that, pollution load is increased due to runoff from agricultural fields, disposal of untreated sewage, salt pan run off, coconut husk retting and lime-shell dredging. Extensive addition of nutrients would neither be economical nor safe from environmental points of view. Hence remedial measures need to be taken for sustainability of the ecosystem.

Key words: Organic carbon, Redox potential, Alkaline, Seasonal patterns, Fluctuating, Dredging

INTRODUCTION

Man made impacts along the coastal ocean and in estuaries has increased rapidly over the last decades affecting the natural dynamic equilibrium and the biotic composition of the respective ecosystems. The main cause of such changes are due to the introduction of untreated sewage which is rich in organic substances and plant nutrients from human settlements, urbanisation and growing industries, leaching of nutrients from soils and agricultural fields and animal husbandry. Sediment nutrients are known to control nutrients of overlying water and regulate the primary productivity. Studies on sediment nutrients are useful in determining sediment-water interactions, which eventually affects organic production. The level of organic carbon in sediments is reported to be a reliable index about the nutrient regeneration and the productivity of a water body. Redox potential is a measure of organic matter within the sediment and its oxidizing or reducing power. Oxidation-reduction activities at the sediment- water interface bear marked influence upon the estuarine chemistry and upon the type of organisms present in the sediment (Anila Kumary *et al*., 2001).

Outflow from agricultural and urban runoff and discharge from sewage outfalls can elevate phosphorus and nitrogen concentrations in estuarine system. Anthropogenic inputs frequently cause excessive eutrophication in the aquatic environment especially in estuaries and coastal regions where the circulation is restricted. Nutrient enrichment in river, lake, ground water and tidal waters are considered to be one of the major environmental issues reported in many countries (Heathwaite *et al*., 1996). It stimulates the growth of plants in water and nutrient enrichment which ultimately leads to the degradation of entire ecosystem if not controlled in a systematic manner. The present study is to assess and characterize the seasonal variation in sediment quality of Manakudy estuary, to understand qualitative and quantitative aspects of sediment nutrients where there is inflow of water from agricultural fields, coconut husk retting, lime-shell dredging, salt pan and untreated sewage. The fluctuation in the composition of sediments and its nature can indicate the stress on shallow aquatic environments (Saraladevi *et al.*, 1992). Thus the study of nutrients in sediments represents a useful tool for determining the actual state of environmental pollution of a water body.

MATERIALS AND METHODS

Study Area

Manakudy estuary (8°4' N latitude and 77°26' E longitude)on the South-west coast of Kanyakumari district has a total area of about 145 ha. extending over 2 Km, bordered with vast stretches of salt pans on either side (Fig. 1). It is a sand built estuary formed by the confluence of river Pazhayar in between East and West Manakudy villages. The estuary is connected with the sea during the rainy season and land locked for the rest of the year by sand bar. The formation and closure of the sand bar at the mouth of the estuary leads to pronounced changes in the composition of sediment nutrients of the estuary. During this investigation seasonal variation in the nutrients of the sediments of estuary have been studied where there is inflow of water from agricultural fields, coconut husk retting, lime-shell dredging, salt pan and untreated sewage.

Ten sampling stations, almost equidistant from one another representing different ecological conditions were chosen for collection of sediments in the Manakudy estuary from estuarine mouth bed to river basin (Fig. 1). Sediment samples were collected during pre-monsoon (April 2011), monsoon (October 2011) and post-monsoon (January 2012) and were transferred separately to clean, dry polythene containers, homogenized well and were brought to the laboratory for analysis. pH and redox potential of samples were taken as soon as the samples were brought to the laboratory using inert platinum electrode connected to pH – E*h* meter (Pearson & Stanley, 1979). EC was determined by conductivity meter. A portion of these samples were air dried and finely powdered using agate mortar. Percentage of OC was determined by titration method (El Wakeel *et al.*, 1957). Total soluble salt (TSS) and sulphate-

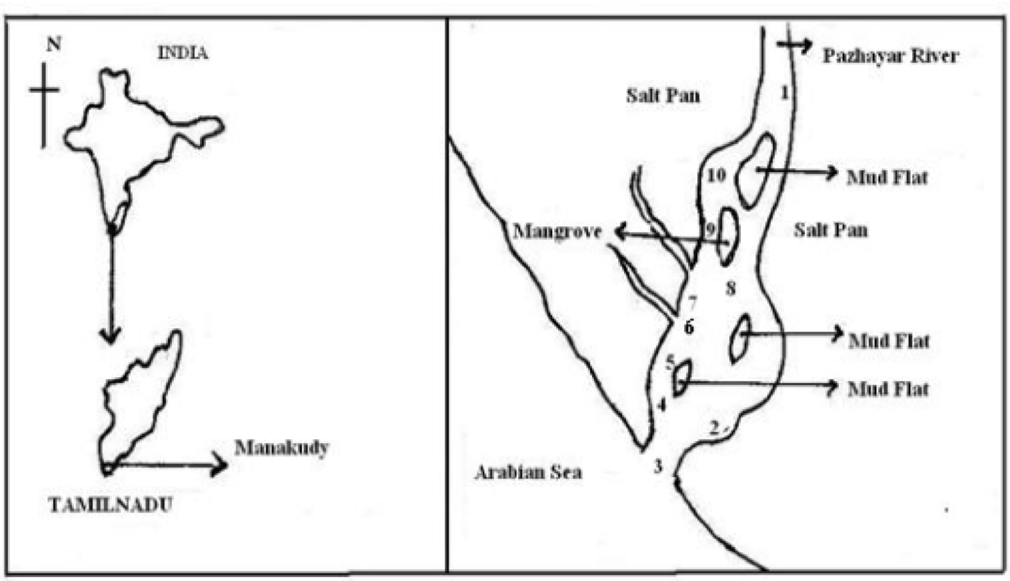


Fig. 1. Location map of the area of study

sulphur were determined using 1: 2.5 water solution. Chloride content was determined by titrating with $AgNO_3$ using potassium chromate indicator. Calcium and Magnesium were estimated by titration with EDTA. Phosphate-phosphorus was determined by Olesen's method using spectrophotometer. Total nitrogen was estimated by modified Kjeldahl method. Sodium and potassium were determined by flame photometer. All the reagents and chemicals used were of analytical grade.

Statistical two-way ANOVA and correlation analyses were applied on the data to find out the inter-relation among different parameters.

RESULTS AND DISCUSSION

Graphical representation for the seasonal variations in the parameters are computed with figures 2 to 14. Correlation matrix of sediment quality parameters for different seasons are given in Tables 1 to 3.

pH: The variation in pH for the sediments collected from the ten stations under study is given in Fig. 2. The sediment pH of the study area varied from 7.48 to 8.3. All the sediment samples were found to be alkaline. The results on the seasonal changes in sediment pH of the experimental stations revealed that it was maximum during the monsoon period and minimum during the non-monsoon period. The lower pH value 7.48 recorded at Station 6 during the pre-monsoon period may be due to the increased rate of decomposition of organic matter and conversion of released CO_2 into carbonic acid. This result is in accordance with earlier reports (Saha, 1985 and Umayoru Bhagan *et al.*, 1998). They reported an increase in pH during rainy season and decrease during summer and their results provide the evidence for the dynamics of hydrogen producing and consuming microbial population. In all the three seasons, pH showed strong negative correlation with redox potential. Two-way ANOVA indicated the variation of pH between the seasons was statistically significant ($F = 10.3389$; $p = 0.001$) but it was statistically non-significant between the stations ($F=1.7118$; $p=0.1585$)

Electrical Conductivity (EC)

EC is directly related to the soluble salt concentration of sediment. It is influenced by industrial effluents, domestic and municipal sewage , salinity intrusion and fresh water influx from rivers (George Sebastian *et al.*, 2012).EC values range from 0.12 mS/cm to 7.56 mS/cm,0.09 mS/cm to 3.62 mS/cm and 0.3 mS/cm to 9.9 mS/cm for sediment samples collected during pre-monsoon, monsoon and post-monsoon seasons respectively. The seasonal variations of EC are shown in Fig. 4. Sample at station 6 showed highest EC value during post-monsoon season. Higher EC value could be due to higher concentration of water soluble ions

Table 1. Correlation matrix of sediment quality parameters during pre-monsoon

	pH	EC	Eh	TSS	OC	N	P	Cl	Ca	Mg	SO_4-S	Na	K
pH	1												
EC	-0.44	1											
Eh	-1	0.429	1										
TSS	-0.44	1	0.428	1									
OC	-0.61	0.711	0.614	0.711	1								
N	-0.71	0.569	0.717	0.569	0.894	1							
P	-0.36	0.019	0.373	0.018	-0.02	0.087	1						
Cl	-0.58	0.833	0.576	0.832	0.891	0.771	-0.09	1					
Ca	-0.52	0.686	0.524	0.686	0.829	0.772	-0.25	0.952	1				
Mg	-0.77	0.731	0.775	0.731	0.881	0.799	0.28	0.868	0.785	1			
SO_4-S	-0.19	0.605	0.203	0.606	0.515	0.629	-0.05	0.642	0.68	0.482	1		
Na	-0.58	0.835	0.581	0.835	0.881	0.759	-0.08	0.999	0.948	0.866	0.63	1	
K	-0.73	0.761	0.733	0.761	0.856	0.814	0.05	0.87	0.785	0.852	0.627	0.865	1

like Na^+, K^+ and Cl^- (Rajanna and Belagali, 2012). Accumulation of soluble salts in sediments may be probably due to sufficient leaching and flushing of salts due to higher rainfall from the nearby salt pan. Sample at station 1 showed lowest EC value during monsoon season. This lowering in EC value may be due to fresh water influx from Pazhayar river to the estuary during the monsoon season.

Redox potential (E*h*)

Redox potential (E*h*) of sediments is a convenient index to understand whether the sediment has reduction potential or not. (Anila Kumary *et al*., 2001). A positive E*h* value results from a state that tends towards oxidation and a negative E*h* indicates a system causing reduction. The seasonal variations of E*h* are given in Fig. 3. The negative values of E*h* recorded at all stations suggest that the sediments were in the reduced state. A high negative value of E*h* during the monsoon indicates that there was degradation of the natural environment due to discharge of sewage water.

Total Soluble Salt (TSS)

TSS present in sediment samples consists of chemical species such as calcium, magnesium, sodium, potassium, chloride, nitrate, carbonate, bicarbonate and heavy metals (George Sebastian *et al*., 2012).TSS content was 0.345% at station 5 during pre-monsoon ,0.166% at station 6 during monsoon and 0.453% at station 6 during post-monsoon. The seasonal variations of TSS are given in Fig. 5. Higher concentration of TSS due to excess soluble salts in sediment cause high osmotic pressure which prevent the absorption of moisture and nutrients by plants in adequate amounts (George Sebastian *et al*., 2012).

Two-way ANOVA of the parameters EC,E*h* and TSS showed that the variations between seasons were significant at 1 % level and were non-significant between the stations ($p > 0.05$).EC showed strong positive correlation with all the nutrients except magnesium. E*h* showed weak negative correlation with all nutrients except chloride, phosphorus and magnesium.TSS showed strong positive correlation with all nutrients.

Organic Carbon (OC)

OC content estimation indicates variations in all the sites (Fig. 6).Enrichment of OC indicates incorporation of organic materials from the river water . Further, OC is a reliable index of nutrient degradation and productivity of the water body (Deleep Packia Raj, 2010).The higher level of OC% during pre-monsoon at stations 5 and 6 is due to high evaporation of water and decomposition of algae while low levels during monsoon is due to lesser evaporation of reservoir water (Anila Kumary *et al*., 2001). Higher percentage of OC exhibited during pre-monsoon may be due to death and decay of leaf litter from the nearby mangrove forest. Minimum available water and poor flow rate may also account for high OC concentration in the sediments during pre-monsoon seasons. Low OC content at station 3 during monsoon season is due to increased flow rate at the bar mouth of the estuary which prevents the settling of organic carbon. The variations of OC between stations and seasons were found to be non-significant ($p = 0.3750$ and 0.1204). In pre-monsoon and in monsoon OC showed strong positive correlation with nitrogen, chloride, magnesium, sodium and potassium whereas in post-monsoon it is positively correlated with nitrogen, phosphorus and sulphate-sulphur.

Chloride

In the present study, chloride concentration varied from 218.8 ppm to 7888.4 ppm,0 ppm to 1239.08 ppm and 172.5 ppm to 7153.84 ppm for sediment samples during pre-monsoon, monsoon and post-monsoon. The seasonal variations of chloride are given in Fig. 7. The high concentration of chloride during pre-monsoon and post-monsoon seasons may be due to disposal of water from the neighboring salt pan. Two-way ANOVA showed that it was significant between seasons and non-significant between stations ($p= 0.00531$ and 0.09983). Chloride showed strong positive correlation with all other nutrients.

Total Nitrogen

Sediment nitrogen recorded in the present study was more at station 6 when compared with the values registered at other stations. The infiltration of fertilizer used in the nearby

Table 2. Correlation matrix of sediment quality parameters during monsoon

	pH	EC	Eh	TSS	OC	N	P	Cl	Ca	Mg	SO_4-S	Na	K
pH	1												
EC	0.3724	1											
Eh	-0.998	-0.388	1										
TSS	0.3736	1	-0.389	1									
OC	0.4399	0.899	-0.451	0.899	1								
N	0.4399	0.899	-0.451	0.899	1	1							
P	-0.309	0.35	0.305	0.35	0.412	0.412	1						
Cl	0.2049	0.959	-0.221	0.959	0.897	0.897	0.482	1					
Ca	0.0995	0.441	-0.1	0.441	0.749	0.749	0.503	0.575	1				
Mg	0.35	0.484	-0.37	0.484	0.477	0.477	-0.22	0.475	0.305	1			
SO_4-S	0.6772	0.446	-0.696	0.447	0.682	0.683	-0.02	0.444	0.568	0.513	1		
Na	0.3459	0.98	-0.361	0.98	0.944	0.944	0.456	0.984	0.576	0.468	0.529	1	
K	0.4641	0.93	-0.479	0.93	0.987	0.987	0.358	0.919	0.668	0.538	0.696	0.962	1

agricultural fields, retting of coconut husk and other anthropogenic activities facilitate an increase in the concentration of nitrogenous material in the sediment (George Sebastian *et al*., 2012). The seasonal variations of total nitrogen are given in Fig. 8. The total nitrogen of sediment was higher during pre-monsoon, due to the decay of a large amount of phytoplankton which settled from the water column (Venkataswamy and Hariharan, 1976). The lower value of total nitrogen during monsoon season may be accounted for the lower level of organic matter (Bragadeeswaran *et al*., 2007). Similar to that of OC, total nitrogen values were higher during pre-monsoon and lower during monsoon. Two-way ANOVA showed variations between stations and seasons were found to be significant at 1% level (p= 0.3750 and 0.1204). OC also showed strong positive correlation with all other nutrients.

Phosphate-Phosphorus

Phosphorus is an important sediment parameter since it acts as a reservoir for phosphorus by retaining

Table 3. Correlation matrix of sediment quality parameters during post-monsoon

	pH	EC	Eh	TSS	OC	N	P	Cl	Ca	Mg	SO_4-S	Na	K
pH	1												
EC	0.065	1											
Eh	-0.99	-0.09	1										
TSS	0.064	1	-0.09	1									
OC	0.315	0.827	-0.35	0.826	1								
N	0.243	0.937	-0.27	0.937	0.965	1							
P	0.334	0.879	-0.37	0.878	0.966	0.967	1						
Cl	-0.08	0.924	0.069	0.925	0.617	0.795	0.693	1					
Ca	0.106	0.89	-0.13	0.891	0.803	0.893	0.866	0.888	1				
Mg	-0.27	0.723	0.284	0.724	0.267	0.5	0.345	0.871	0.574	1			
SO_4-S	0.025	0.943	-0.04	0.944	0.883	0.946	0.924	0.853	0.935	0.561	1		
Na	0.022	0.919	-0.04	0.92	0.631	0.804	0.685	0.977	0.846	0.846	0.814	1	
K	0.145	0.939	-0.172	0.939	0.741	0.874	0.772	0.935	0.859	0.739	0.847	0.98	1

Fig 2.Seasonal variation of pH

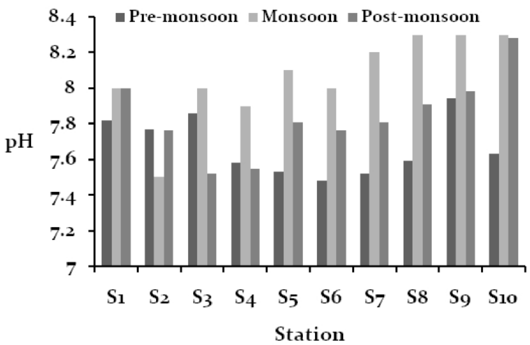


Fig 3.Seasonal variation of Eh (mV)

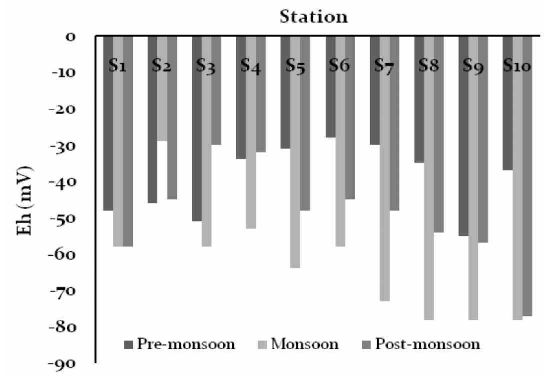


Fig 4.Seasonal variation of EC(mS/cm)

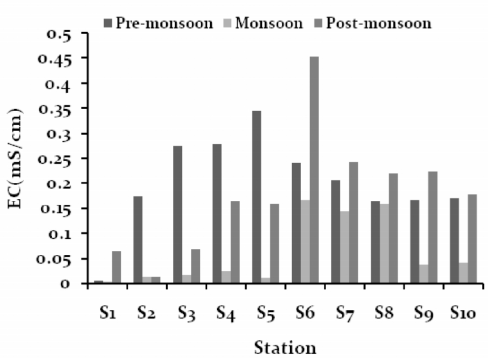


Fig 5.Seasonal variation of TSS(%)

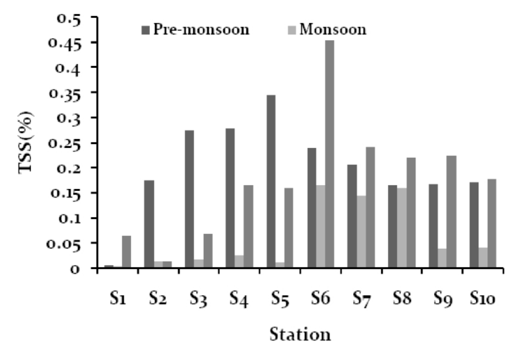


Fig 6.Seasonal variation of OC(%)

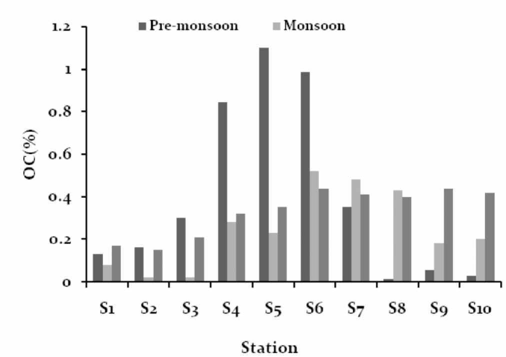


Fig 7.Seasonal variation of Chloride(ppm)

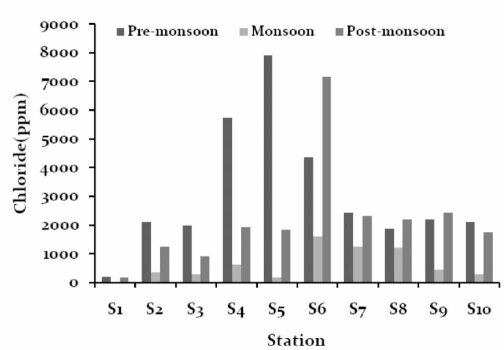


Fig 8. Seasonal variation of Nitrogen(ppm)

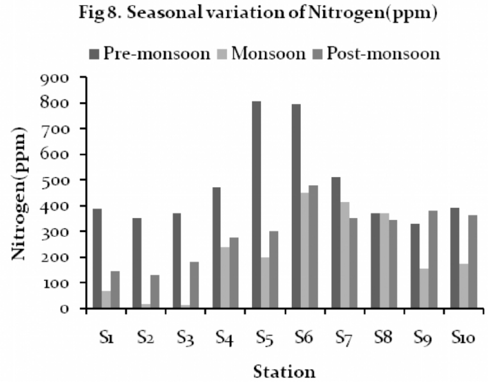


Fig 9.Seasonal variation of Phosphorus(ppm)

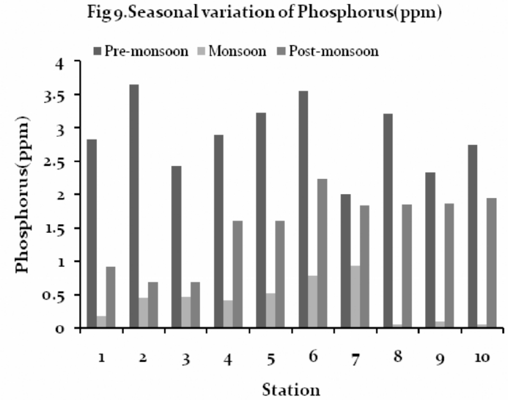


Fig 10. Seasonal variation of Calcium(ppm)

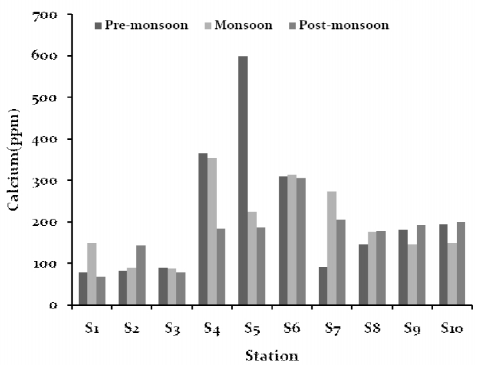


Fig 12.Seasonal variation of Sulphate(ppm)

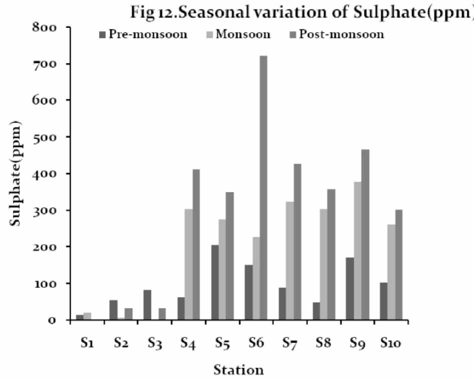


Fig 14. Seasonal variation of Potassium(ppm)

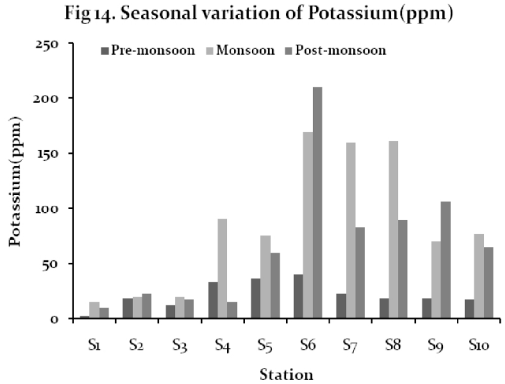


Fig 11. Seasonal variation of Magnesium(ppm)

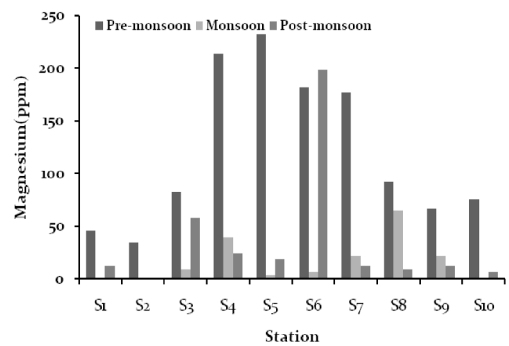
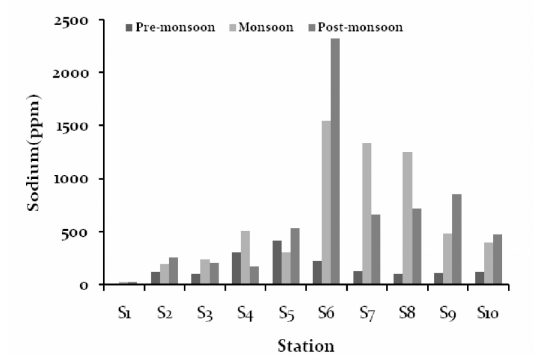


Fig 13.Seasonal variation of Sodium(ppm)



it through adsorption and releasing it to the over lying water under favourable conditions. The increased load of phosphorus derived from agricultural land and sewage has a crucial role in the eutrophication processes (George Sebastian *et al.*, 2012). The continuous adsorption and desorption of phosphates by sediments serve both as a source and sink for phosphate in phosphorus cycle(Nair *et al.*, 1993). The seasonal variations of phosphorus are given in Fig. 9.The high concentration of chloride Higher concentration of phosphorus at station 6 is due to the agricultural waste discharge from the paddy fields of the nearby region, urban sewage and coconut husk retting activities. Phosphorus in the sediment was found high during pre-monsoon and post-monsoon at station 6 (3.55 ppm and 2.32 ppm respectively) and low (0.05 ppm) at stations 8 and 10 during monsoon. The higher values were due to the dead organic matter settling from top and are related to the permeability of the sediment (Bragadeeswaran *et al.*, 2007). Further maximum concentration of phosphorus was due to phosphate containing fertilizers washed off from agricultural fields. Lower values of phosphate during monsoon may be due to the removal of top layer of sediment by heavy flood and deposition of sand. Two-way ANOVA showed the variations were significant between seasons and non-significant between stations. Phosphorus showed a weak positive correlation with other nutrients except calcium and sulphate-sulphur in post-monsoon season.

Calcium and Magnesium

Calcium and magnesium are the two most abundant alkaline components in sediment. Calcium present in high concentration in the rock is leached by water which contaminate the water. Disposal of sewage and industrial effluents impart calcium which has great affinity towards the soil particle and in turn affects the soil texture (Sobha *et al*., 2008). Calcium and Magnesium occur in nature as its carbonates, phosphates, sulphates or silicate minerals. In the sediment samples the calcium value ranged from 79.5 ppm (Station 1) to 599.2 ppm (Station 5) during pre-monsoon, 88.10 ppm(Station 3) to 355.05 ppm (Station 4) during monsoon and 68.03 ppm (Station 1) to 306.6 ppm (Station 6) during post- monsoon seasons. The maximum calcium content observed at station 5 and 4 may be due to the leaching of dead shelled organisms. The seasonal variations in calcium content of the sediments are given in Fig. 10.The excess amount of calcium however decreases the availability of many macro nutrients (Rajanna and Belagali, 2012). Two-way ANOVA showed for calcium the variations were significant between stations at 1% level and non-significant between seasons (p=0.6226).

Magnesium concentration for sediment samples varied from 34.4 ppm (Station 2) to 213.8 ppm (Station 4), 0 ppm (Stations 1, 2 & 10) to 64.512 ppm (Station 8) and 0 ppm (Station 2) to 199.09 ppm (Station 6) during pre-monsoon, monsoon and post –monsoon seasons respectively. The seasonal variations of magnesium are given in Fig. 11.The inorganic carbonates occur primarily as sparingly soluble alkaline earth carbonates such as calcium carbonates and dolomites (Rajanna and Belagali, 2012). Two-way ANOVA showed for magnesium the variations were significant between seasons and non-significant between stations (p=0.1982).

Sulphate-Sulphur

Sulphate concentration in sediments play an important role in the release of phosphorus which leads to eutrophication in estuaries (George Sebastian *et al*., 2012). Under anoxic conditions, sulphate reduction takes place and promotes the release of phosphorus from sediments (Roden and Edmonds, 1997). This results in an increase of phosphorus in the water column and subsequently eutrophication. Sulphate concentration for sediment samples varied from 13.7 ppm(Station1) to 206 ppm (Station 5), 4.81 ppm(Station 2) to 377.68 ppm(Station 9),0 ppm(Station 1) to 721.03 ppm (Station 6) during pre-monsoon, monsoon and post-monsoon seasons respectively. The seasonal variations of sulphate are given in Fig. 12. Maximum level may be due to the enriched applications of sulphur containing fertilizers in the nearby agricultural fields and also due to the inflow of water from coconut husk retting pits. Two-way ANOVA showed that the variations were significant between seasons and stations (p= 0.002124 and 0.005).

Sodium and Potassium

Sodium is an important constituent in sediment. The carbonate, sulphate, nitrate and chloride of sodium are found abundantly in nature. The seasonal variations of sodium are given in Fig. 13. The season wise analysis of sodium showed that its value ranged from 7.4 ppm (Station 1) to 413.8 ppm (Station 5), 27.25 ppm (Station 1) to 1543.52 ppm (Station 6) and 21.87 ppm (Station 1) to 2324.2 ppm (Station 6) during pre-monsoon, monsoon and post-monsoon seasons respectively. The maximum value of 2324.2 ppm was observed at station 6 (post-monsoon) and minimum of 7.4 ppm was observed at station 1 (pre-monsoon). The maximum value of 2324.2 ppm reported at station 6 (post-monsoon) indicates high degree of pollution due to the intervenes of human activities, inflow of water from salt pan and the application of fertilizers in the adjacent fields. In general, industrial effluents and domestic sewage are rich in sodium which increases its presence in the natural water, when they are disposed into natural water (Trivedi and Goel, 1986).

Like sodium, potassium is also a naturally occurring constituent in sediment. The major source of potassium in fresh water is due to weathering of rocks. But the quantity increases in the polluted water due to the mixing of domestic wastes (Sobha *et al*., 2008). The seasonal variations of potassium are given in Fig. 14. The potassium content in the sample ranged from 2.5 ppm (Station 1) to 39.7 ppm (Station 6),14.87 ppm (Station 1) to 169.29 ppm (Station 6) and 9.720 ppm (Station 1) to 210.17 ppm (Station6) during pre-monsoon, monsoon and post-monsoon seasons respectively. The maximum value of potassium was found at station 6 in all the three seasons indicate that out of the ten stations selected the site 6 was the most polluted station where there is inflow of untreated sewage and inflow of water from agricultural fields. Two-way ANOVA showed that the variations of sodium and potassium were significant between seasons and stations at 1% level (p= 0.002124 and 0.005). Further sodium showed a strong positive correlation with potassium at all seasons.

CONCLUSIONS

Based on the above experimental results and discussions, the present study clearly indicates that the estuarine sediments are contaminated. During pre-monsoon and post-monsoon seasons, most of the samples show higher concentration of nutrients. Thus, nutrients concentration are fluctuating from season to season , which implies that pollution load is increased due to industrialization and run off from the agricultural fields. So, extensive addition of nutrients would neither be economical nor safe from environmental points of view. Further higher nutrient concentration is associated with lower oxygen content and higher salinities. This would affect fish and shell fish production. The nutrient supply can initiate eutrophication in the estuary. Hence, the distribution pattern of nutrients in this estuary is controlled by many factors like estuarine dynamics, effluent discharges from urban, agricultural and industrial sources, coconut husk retting, fish processing unit etc.

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