4. SEDIMENT ANALYSIS

4.1. INTRODUCTION

In an aquatic system, the sediments act as a storage reservoir of nutrient materials for water. In the estuary the sediments are deposited through river runoff, agricultural byproducts, industrial and domestic waste (Daskalakis and O'Connor, 1995). The estuary is a source of sediment for the open-coast system and acts as a transitional environment for sediment to reach the open coast from terrigenous origins (Davis and Fitz Gerald, 2004). Estuarine sediment and water are characterized by specific and complex physical, chemical and microbiological properties. These properties interact with each other and collectively constitute a unique environment to the organism. Turbulent mixing of fresh water and seawater can generate rapid changes in Eh, pH, salinity and trace element concentrations (Balachandran *et al.,* 2006). The river runoff water carries nutrients as well as many toxic substances such as pesticides from nearby fertilized farmlands to the estuary (Krauskopf, 1956).

The studies on the chemical characteristics of the estuarine sediments are useful in assessing the water quality and management of ecosystem. The sediments mainly govern the nutrient economy of an aquatic ecosystem and knowledge on the role of sediment nutrients is especially useful in determining the sediment water interactions, which eventually affect the productivity (Nair *et al.*, 1984). Sediment analysis of aquatic environment has drawn greater attention in the world's scientific scenario due to growing awareness of environmental

pollution and its impact on ecosystem. The most important raw materials for plant productivity in aquatic systems are organic and inorganic forms of carbon, nitrogen, phosphate, and micronutrients (Santhosh *et al*., 2008).

The physicochemical character of sediments regulates food and feeding habits and other life activities of benthic forms to a great extent (Ramachandra *et al*., 1984). Sediments rich in organic matter act as good sources of nutrients. The replenishment of these nutrients greatly helps in the biogeochemical cycle of the system. Such an exchange of nutrients depends upon the characteristics of the sediment and the hydrographic features of the estuary (Pomeroy *et al.,* 1965).The three important elements carbon, nitrogen and phosphorus are underlying various biogeochemical processes, which affect the productivity of the ecosystem (Ghosh and Choudhury, 1989). Nitrogen is probably the major regulatory nutritional factor in most detritus based system (Tennore, 1981). Nitrogen and phosphorus compounds accumulate in estuarine sediments through coagulation and sedimentation of suspended particles delivered to the estuary. Sediments normally have significantly higher concentrations of nutrients relative to the water column (Congdon and Mc Comb, 1980). Sediment adsorption of N and P may account for much of the available nutrients, with adsorbed to interstitial ratios of 30:1 for NH_4-N concentrations and 270:1 for PO_4-P concentrations (Udy and Dennison, 1996).

Trace metals entering into the estuarine system do not remain in water but form a part of sediment and re-enter into water by various physical, chemical and biological processes. Thus the sediments act as buffer. Sediments also

determine the quality of water. The chemical environment of water and sediment differ significantly (Madhukumar and Anirudhan, 1995). Studies on the organic matter in sediments indicate the extent of biological activity and indirectly the fertility of overlying seawater as well as the pollution of the water (Alagarsamy, 1991).

The level of organic carbon in sediments is reported to be a reliable indicator of nutrient regeneration and the productivity of the water body (Anila Kumary *et al.*, 2001). Organic carbon in riverine and estuarine sediments is controlled mostly by the rate of organic to inorganic constituents, primary productivity, composition and texture of the sediments. Textural control over total organic carbon is indicated by the correlation of total organic carbon with sand, silt and clay percentages of the sediments. Association of total organic carbon with clay minerals is of particular significance in estuarine sediments (Muraleedharan Nair and Ramachandran**,** 2002).

Sediments are increasingly recognized as both a carrier and a possible source of contaminants in aquatic systems and these materials may also affect groundwater quality and agricultural products when disposed on land. Contaminants are not necessarily fixed permanently by the sediment, but may be recycled via biological and chemical agents both within the sedimentary compartment and the water column. Bioaccumulation and food chain transfer may be strongly affected by sediment-associated proportions of pollutants. Sediment has aptly been called as Trace element trap (Eugenia *et al.,* 2004; Chester and Dooley, 1979) because they eventually receive almost all the heavy

metals, which enter the aquatic environment (Karthikeyan *et al.,* 2007). Trace metals are essential micronutrients for organisms at optimum levels but toxic at higher levels to animals and human beings (Forstner and Wittmans, 1979).

Sediments are major repositories for metals and besides providing the environmental status. They are also used to estimate the level of pollution in a region (Burton and Scott, 1992; Caccia *et al*., 2003). Mining and smelting, combustion of fossil fuels, waste disposal from processing and manufacturing industries and municipal sewage disposal contribute heavy metals to the coastal environment and thus the coastal waters become polluted by metals. Estuaries are also being used on a large scale for the waste disposal. As a result, pollution of estuaries especially with heavy metals has become a serious problem in recent times (Supte and Gaykar, 1992). In aquatic environments, many heavy metals are transported predominantly in association with particulate matter and consequently a high concentration of heavy metals is often detected in sediments in many industrialized harbors and coastal regions around the world (Miller *et al*., 2000; Chen *et al*., 2001; Feng *et al*., 2004; Wang *et al*., 2007). Variability in metal concentrations of marine organism depends on many factors, both environmental and purely biological (Phillips, 1995). Estuaries can act as a "geochemical reactor" changing the chemical forms (Chiffoleau *et al*., 1994) of continental derived trace metals. The study of sediments represents a useful tool for determining the actual state of environmental pollution of a water body. Sediments are also the site for a suite of different biogeochemical processes that determine the ultimate fate of nutrients within the estuary.

Studies on the physicochemical aspects have been made in the sediments of different Indian estuaries. Important works on the physicochemical factors of sediments along the west coast has been done by Singbal (1976), Shirodkar and Sengupta (1985), Nasnolkar *et al*. (1996) and Fernandes and Nayak (2009) in the Mandovi estuary; Dessai and Nayak (2007) in Zuari estuary; Sankaranarayanan and Panampunnayil (1979), Remani *et al*. (1980), Nair *et al*.(1993) and Seralathan *et al*. (1993) in Cochin backwaters; Tulaskar *et al*. (1992) in the Rajapur and Vagothan estuaries; Regunath *et al*. (1995) in the Tellicherry mangrove sediments; Bijoy Nandan and Azis (1996), Santhosh *et al*. (2008) in Paravur Kappil backwater; Harikumar *et al*. (2009) in Vembanad wetland system; Anju kumar *et al*. (2011) in Cochin estuary. Prema (2000), Selvamohan (2006) and Mohideen Askar Nawas (2009) in the Rajakkamangalam estuary, Vetha Roy and Chandrasekar (2007) in the Tambraparani estuary, Vasantha (2004) and Kumaraswamy (2005) in Thengapattinam estuary. Sukumaran (2002), Taradevi (2002), Indirani (2003), Sugirtha Kumar and Edward Patterson (2009), Rashi *et al*. (2007) and Jeena Pearl (2010) in Manakudy estuary.

Studies on sediments along the east coast of India were performed by Venkateswaran and Natarajan (1983) on the distribution of free phosphate in the sediments of Porto Novo, Sivakumar *et al*. (1983) studied seasonal variations in carbon, nitrogen and phosphorus in sediments of the Vellar estuary. Chemical and sediment characteristics of the upper reaches of the Cauvery estuary were done by Ramanathan *et al*. (1988). Muraleedharan Nair and Ramachandran(2002) in Beypore estuary, Anathan *et al*. (2005) in Ariyankuppam estuary and Bragadeeswaran *et al*. (2007) in Arasalar estuary.

Environmental significance in recent sediments along Bay of Bengal and Palk Bay was studied by Sundararajan and Natesan (2010). Concentration of nutrients and C: N: P ratio in surface sediments of a tropical coastal lagoon complex affected by agricultural runoff was studied by De la Lanza *et al*. (2011). The present investigation deals with the studies of physicochemical parameters of sediments in selected stations of Thengapattinam estuary.

4.2. MATERIALS AND METHODS

Surface sediments samples in triplicate were collected monthly from each fixed sampling stations using a Van Veen Grab. The samples were transferred into cleaned labeled polythene bags and transported to laboratory in an icebox and later thawed, dried at 50-60°C. pH and electrical conductivity of the sediment were recorded immediately after the collection of sediment samples.

4.2.1. DETERMINATION OF SEDIMENT pH

The pH of the sample was determined by using the pH meter (Potentiometric method). Various standard buffer solutions with 4.0, 7.0 and 9.2 pH were used for the standardization of the pH meter.

20 gm of the sediment sample was taken in a 100 ml glass beaker. To this 4 ml of distilled water was added, stirred well and kept for half an hour with an intermediate stirring. Then the pH of the sample was determined using the pH meter.

4.2.2. DETERMINATION OF ELECTRICAL CONDUCTIVITY

Electrical conductivity was measured using conductivity bridge. For this, 0.01 N KCl solutions were used as reference solution. The unit measured was ds/m. 20 gm of the sample was taken in a 100 ml glass beaker. To this 40 ml of distilled water was added. It was stirred well and kept for half an hour with intermediate stirring. Then electrical conductivity of the sample was determined using the conductivity bridge.

4.2.3 ESTIMATION OF TOTAL NITROGEN (AOAC, 1965)

Sediment sample was weighed by an electronic balance to the tune of around one gram. The exact weight was noted to the fourth digit in mg. The weighed sample was kept in the digestion flask carefully without spilling. Then 0.7 gm of $CuSO_4$, 15 gm of powered K_2SO_4 and 25 ml of concentrated H_2SO_4 were added. H_2SO_4 was added in such a way that the sample particles were not at the neck portion of the flask and went down to the bottom of the digestion flask which was placed in an inclined position. It was heated until frothing ceased. A small amount of paraffin was added to reduce frothing. This was boiled briskly until the solution become clear and continued boiling for another 30 minutes longer. It was allowed to cool after taking out from the fume chamber. 200 ml of distilled water was added to digestion flask and the content was further cooled below 25°C. Then the flask was placed on the distillation table and a layer of NaOH, 25 gm of solid reagent or 40% NaOH solution were added. Care was taken to add the NaOH solution without agitation to avoid the loss of NH_3. The flask was immediately connected to the distillation bulb and to the condenser with the tip of the condenser immersed in standard acid (0.5N H_2SO_4) in the receiver and then the flask was rotated to get the contents thoroughly mixed until all the NH_3 was distilled. The excess standard acid in the distillate was titrated with standard NaOH (0.5N) using methyl red as indicator and at last it was corrected for blank determination on reagent

$$\% \text{ of N} = \frac{(\text{A. Na} - \text{B. Nb}) \times 0.01401 \times 100}{W}$$

Where,

A   =   ml of Standard $H_2 SO_4$ used

B   =   ml of standard NaOH used

Na   =   Normality of standard H_2SO_4

Nb   =   Normality of standard NaOH

W   =   Weight of the sample taken

4.2.4 ESTIMATION OF AVAILABLE PHOSPHORUS

Olsen's method – Olsen *et al*. (1954) and Watanabe and Olsen (1965)

5 gm of sediment sample was taken in a 250 ml conical flask, one teaspoon of carbon black was added (Dargo G. 60) followed by 50 ml of Olsen's reagent. The contents were shaken for 30 minutes on a platform type shaker. The suspension was filtered through whatman No. 1 filter paper. More activated carbon was added if necessary to obtain a clear filtrate. The flask was shaken immediately before pouring the suspension into the funnel. If turbid filtrate was noticed, more filter papers were used while filtering; the suspension was poured to the maximum level of the 5 cm funnel with filter paper only once. Pouring was avoided second time.

Colour development

5 ml of the filtrate was pipetted out into a 25 ml volumetric flask. The solution was acidified carefully in the volumetric flask with 5N H_2SO_4 to pH 5.0. This can be easily done by taking 5 ml of sodium bicarbonate in a separate 25 ml standard flask and determine the volume of acid required to bring the pH of the solution to 5.0 using P-Nitrophenol indicator. The yellow colour of this indicator

disappeared when the pH was brought down to 5.0 by the addition of H_2SO_4 (5N).The quantity of acid thus determined may be added to individual aliquot pipetted out. After the adjustment of pH, the contents were diluted to 20 ml with distilled water. 4 ml of the reagent B was added (freshly prepared) and made up to volume of 25 ml with distilled water. It was shaken well to make it homogenous and waited for 10 minutes. The intensity of the blue colour was measured by photoelectric colorimeter using 660 nm filter (red filter) against a blank.

Calculation

Available phosphorous = ppm of ' p' or P_2O_5 in solution as per standard curve.

4.2.5 ESTIMATION OF POTASSIUM (Basheer Ahamed *et al*., 1992)

5g of sediment sample was weighed and transferred into a 100 ml conical flask. Then 25 ml neutral ammonium acetate solution was added, shaken the contents in a horizontal shaker for 5 minutes in a medium speed. The entire solution was filtered through Whatman No.1 filter paper into a 50 ml beaker. The filtrate was fed to the flame photometer through the capillary tube. Earlier, different known concentrations of potassium solution were separately fed into the meter ranging from 10 ppm to 100 ppm. A standard curve was drawn plotting concentration in X- axis and meter reading in Y-axis for potassium. Using this standard graph, potassium content in the sediment sample was measured.

Reagents required

1. Neutral normal ammonium acetate (pH 7.0)

77.0 g of ammonium acetate was dissolved in 900 ml of distilled water and was shaken well. The pH was adjusted either with ammonia or acetic acid and then

it was made up to 1 litre with distilled water.

2. Standard potassium solution

0.1907 of KCl was dissolved in distilled water and was made up to one litre with distilled water.

Calculation

Concentration of potassium in ppm = ppm corresponding to meter reading

4.2.6. DETERMINATION OF ORGANIC CARBON (WALKLEY – BLACK METHOD, 1947)

The sediment sample was weighed to the nearest milligram of 100 to 500 g into a clean, dry, 500 ml Erlenmeyer flask and added exactly 10 ml of the standard dichromate from a burette and swirled gently. Then 20 ml of concentrated sulphuric acid was added rapidly into the solution and immediately mixed by swirling gently at first and then vigorously for a total of 1 minute. The flask was set on an asbestos sheet for 30 minutes. After that, 200 ml water was added and 10 ml orthophosphoric acid was mixed and let to cool. Finally, 0.5 ml of oxidation- reduction indicator was added and titrated against the ferrous solution. The change of colour at the end point was blue to red for the ferroin

indicator and dull green through turbid blue to a brilliant green for the diphenylamine indicator.

$$\text{\% of organic carbon} = \frac{\text{Blank T.V.} - \text{Sample T.V}}{\text{Blank T.V} \times \text{Wt of Sample}} \times \text{ml of N dichromate} \times 0.003 \times \frac{1}{0.77} \times 100$$

Where,

        T.V = Titre value

4.2.7. DETERMINATION OF AVAILABLE COPPER, ZINC, MANGANESE AND IRON (LINDSAY AND NORVEL, 1978)

Reagents and extracting solution

  i. DTPA = 0.0005 M (Formula weight 393.35)

 ii. $CaCl_2$. 2 H_2O = 0.01M solution

iii. TEA = O.1M solution

To prepare 1 litre of DTPA extracting solution, 13.1 ml reagent grade TEA, 1.967 g DTPA (AR grade) and 1.47 g of $CaCl_2$ were dissolved in 100 ml of glass-distilled water. It was left some time for the DTPA to dissolve and was diluted to approximately 900 ml. Then the pH was adjusted to 7.3 ± 0.5 with 1:1 HCl while stirring and was diluted to one litre. Addition of approximately 4 ml HCl (0.1N) brought the pH of the solution to 7.3.

Extraction and determination

10 g of air dried sediment was weighed in a 125 ml conical flask. Then 20 ml of the DTPA extracting solution was added. The flask was corked and placed upright on a horizontal shaker. It was shaken for two hours at a speed of 129

cycles per minute. The suspension was filtered through Whatman No. 42 filter paper. The filtrate was kept in the polypropylene bottles and analyzed for Cu, Zn, Mn and Fe with an Atomic adsorption Spectrophotometer (AAS).

4.3. RESULT

The physicochemical parameters of the sediment are recorded in the sampling stations during the study periods and are presented below.

4.3.1 pH

The monthly fluctuation and average pH recorded in the sampling stations (S-I to S-III) during 2010 and 2011 are shown in Tables 4.1 and 4.2; Fig.4.1 and 4.2. During 2010, in S-I, the sediment pH varied from a minimum of 6.0 to a maximum of 8.9 in April and November respectively. In S-II, the pH ranged from a minimum of 5.7 in April to a maximum of 8.84 in August and in S-III, it varied from 5.9 in April to 7.9 in August. The maximum monthly average value was recorded in S-I with 7.85±0.80 and it was minimum (6.94±0.65) in S-III. During 2011, in S-I, the sediment pH fluctuated with a minimum of 7.16 in July to a maximum of 8.95 in November. In S-II, the pH ranged from 4.03 in March to 8.2 in November and in S -III, it varied from 4.96 in February to 7.95 in August. The maximum monthly average pH was recorded in S-I with 8.06 ±0.56 against the minimum of 6.82±1.22 in S-II.

Table 4.3 provides seasonal variations in sediment pH during the study period. In the non monsoon period of first year (2010), the minimum pH recorded was 6.15±0.17 in S-III and the maximum was 7.10±0.77 in S-I. In the second year (2011), minimum pH was 5.69±1.12 in S-II and the maximum was 7.85±0.49 in S-I. In 2010, during the southwest monsoon period the minimum pH noticed was 7.12±1.26 in S-II against the maximum of 7.96±0.60 in S-I. In 2011, the minimum pH registered was 6.94±0.72 in S-III against the maximum of

7.72±0.53 in S-I. During the northeast monsoon period of 2010, the minimum value registered was 7.30±0.39 in S-III and the maximum of 8.50±0.29 was noticed in S-I. In the same season during 2011, minimum pH recorded was 7.48±0.47 in S-III and the maximum (8.6±0.25) was noticed in S-I.

Statistical analysis by two-way ANOVA (Table4.3.a) for the data on sediment pH as a function of sampling stations and seasons revealed that the variations between stations and seasons were statistically significant ($F = 19.37$ and 7.677; $P < 0.01$ and $p < 0.05$, $F = 28.20$ and 7.121; $P < 0.01$ and $p < 0.05$) during the study period.

pH showed a significant positive correlation ($P < 0.05$) with copper at S-II and S-III and with potassium and iron at S-III and a significant negative correlation ($P < 0.05$) with electrical conductivity at all stations during 2010. In 2011, pH showed a significant positive correlation ($P < 0.05$) with copper at S-I and S-II, with potassium and phosphorus at S-II and with iron at S-III and a significant negative correlation ($P < 0.05$) with electrical conductivity at S-II (Tables.4.13 to 4.18).

4.3.2 ELECTRICAL CONDUCTIVITY (EC)

The monthly fluctuation and average EC recorded in the sampling stations during 2010 and 2011 are shown in Tables 4.1 and 4.2; Fig.4.3 and 4.4. During 2010, in S-I, the EC values varied from a minimum of 0.044 ds/m to a maximum of 0.64 ds/m in September and April respectively. In S-II, the EC ranged from a minimum of 0.08 ds/m in August to a maximum of 1.07 ds/m in March and in S-III, it varied from 0.078 ds/m in September to 0.49 ds/m in March. The maximum

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monthly average values recorded in S-II was 0.43±0.34 ds/m against the minimum of 0.24±0.14 ds/m in S-III. During 2011, in S-I, the EC fluctuated with a minimum of 0.045 ds/m in October to a maximum of 0.775 ds/m in January. In S -II, the EC ranged between 0.11 ds/m in August and 0.577 ds/m in January; whereas, in S -III, it varied from 0.088 ds/m in October to 0.473 ds/m in February. The maximum monthly average EC was recorded in S-II with 0.32 ±0.17 ds/m and it was minimum (0.22±0.13 ds/m) in S-III.

Seasonal variations in sediment EC noticed in the sampling stations are presented in Table 4.4. In 2010, during non monsoon season a minimum EC of 0.39±0.11 ds/m was recorded in S-III against the maximum EC of 0.845±0.16 ds/m in S-II. In 2011, S-III registered a minimum EC of 0.28±0.13 ds/m and a maximum EC of 0.57±0.20 ds/m in S-I. In 2010, during southwest monsoon season the minimum EC of 0.15±0.08 ds/m was recorded in S-III against the maximum of 0.272±0.26 ds/m in S-II. In the same season during 2011, the minimum value registered was 0.128±0.02 ds/m in S-I and the maximum was 0.19± 0.07 ds/m in S-III. During the northeast monsoon period a minimum EC of 0.103±0.09 ds/m was recorded in S-I and the maximum of 0.182±0.09 ds/m in S-II in 2010. In the second year (2011) of the same season the minimum EC noticed was 0.181±0.17 ds/m in S-I and the maximum was 0.295±0.14 ds/m in S-II.

Statistical analysis by two-way ANOVA (Table4.4.a) for the data on sediment EC as a function of sampling stations and seasons revealed that the variation between stations was statistically not significant (F = 2.527 and 0.85; P

> 0.05) during 2010 and 2011; whereas variation between seasons was statistically significant (F = 11.109 and 7.086; P < 0.05) during the study period.

Electrical conductivity showed a significant negative correlation (P < 0.05) with pH, phosphorus and iron at all stations, with potassium at S-II and S-III and with zinc at S-I in 2010. During 2011, it showed a significant negative correlation (P < 0.05) with phosphorous at all stations, with potassium and zinc at S-I and S-II, with iron at S-II and S-III and with organic carbon and nitrogen at S-III (Tables.4.13 to 4.18).

4.3.3 NITROGEN

Tables 4.1 and 4.2; Fig.4.5 and 4.6 represent the monthly average nitrogen content of sediment samples recorded during the present investigation from the sampling stations. In 2010, the nitrogen content in S-I ranged from 6.03 ppm in March to 18.10 ppm in October. In S-II, the nitrogen ranged from a minimum of 8.62 ppm in March to a maximum of 24.99 ppm in October and in S-III, the range was from 10.34 ppm in September to 23.27 ppm in June. The monthly average nitrogen content was maximum in S-III with 15.80±4.01 ppm and minimum in S-I with 11.78 ±3.90 ppm. In 2011, the nitrogen content ranged from a minimum of 6.21 ppm in January to maximum of 18.96 ppm in the month of June. In S-II, the minimum nitrogen content was 6.88 ppm in March and the maximum (24.14 ppm) was in July. In S-III, the nitrogen content ranged from a minimum of 7.76 ppm in February to a maximum of 22.41 ppm in October. The monthly average nitrogen content was maximum in S-II with 15.26±4.80 ppm and minimum in S-I with 11.9±3.90 ppm.

Seasonal variations in sediment nitrogen content in the sampling stations are shown in Table 4.5. In 2010, the non monsoon period showed minimum nitrogen of 9.04 ±3.02 ppm in S-I and a maximum of 14.22±2.9 ppm in S-III. The southwest monsoon period showed a minimum of 12.92±2.50 ppm in S-I and a maximum of 17.02±5.04 ppm in S-III. During the northeast monsoon period minimum nitrogen content was noticed in S-I with 13.36±5.10 ppm against the maximum of 17.37±5.57 ppm in S-II. In 2011, the non monsoon period showed a minimum of 9.42±3.01 ppm in S-I and a maximum of 13.57±5.77 ppm in S-III. During southwest monsoon, minimum mean nitrogen content of 13.35±5.38 ppm in S-I and the maximum of 17.45±5.50 ppm in S-II were registered. During the northeast monsoon period, the minimum value was in S-I (12.92±2.5 ppm) against the maximum of 17.02 ±4.12 ppm in S-III.

Statistical analysis by two-way ANOVA (Table4.5.a) for the data on sediment nitrogen as a function of sampling stations and seasons revealed that the variation between stations (F = 16.11 and 8.638; P < 0.05) and also between seasons (F = 11.876 and 7.334; P < 0.05) were statistically significant during 2010 and 2011.

In 2010, nitrogen content of the sediment samples showed a significant positive correlation (P < 0.05) with organic carbon at all stations, with potassium at S-I, zinc at S-I and S-III, manganese at S-I and S-II and with phosphorus at S-III. In 2011, it showed a significant positive correlation (P < 0.05) with organic carbon and zinc at all stations, with phosphorus at S-I and S-III and with

potassium and iron at S-I. On the other hand it showed a significant negative correlation (P < 0.05) with electrical conductivity at S-III (Tables.4.13 to 4.18).

4.3.4 PHOSPHORUS

The monthly fluctuation and average phosphorus recorded in the sampling stations during 2010 and 2011 are shown in Tables 4.1 and 4.2; Fig.4.7 and 4.8. During 2010, in S-I, the phosphorus values varied from a minimum of 0.01 ppm to a maximum of 0.18 ppm in January and June respectively. In S-II, the phosphorus ranged from a minimum of 0.012 ppm in January to a maximum of 0.176 ppm in July and in S-III, it varied from 0.06 ppm in January to 0.161 ppm in July. The maximum monthly average values recorded in S-III was 0.114 ±0.03 ppm against the minimum of 0.069±0.05 ppm in S-I. During 2011, in S -I, the phosphorus fluctuated with a minimum of 0.01 ppm in April to a maximum of 0.15 ppm in October. In S- II, the phosphorous ranged from a minimum of 0.022 ppm in April to a maximum of 0.175 ppm in October; whereas, in S-III, it varied from 0.05 ppm in January to 0.16 ppm in August. The maximum monthly average phosphorus recorded in S-III was 0.106 ±0.04 ppm and a minimum of 0.075±0.05 ppm was noticed in S-I.

Table 4.6 provides seasonal variations in sediment phosphorus during the study period. In 2010, during non monsoon season minimum phosphorus of 0.025±0.01 ppm was recorded in S-I; whereas, the maximum phosphorus of 0.095±0.02 ppm was noticed in S-III. In southwest monsoon season the minimum phosphorus of 0.12±0.06 ppm was recorded in S-I against the maximum of 0.145±0.04 ppm in S-III. In northeast monsoon period minimum phosphorus of

0.06±0.02 ppm was noticed in S-I and the maximum of 0.10±0.03ppm was registered in S-III. In 2011, during non monsoon period a maximum phosphorus content of 0.059±0.01ppm was registered in S-III and a minimum value of 0.018±0.008 ppm was noticed in S-I. In southwest monsoon period the minimum value noticed was 0.093±0.02 ppm in S-I and the maximum (0.127±0.04 ppm) was in S-III. In northeast monsoon period the minimum value recorded was 0.115±0.03 ppm in S-I and it was maximum (1.13±0.02 ppm) in S-III.

The two-way ANOVA test (Table4.6.a) revealed that the variations in phosphorus content of sediment between stations (F = 10.16 and 15.07; P < 0.05) and also between seasons (F = 28.45 and 129.27; P > 0.01 and P > 0.001) were statistically significant during 2010 and 2011.

Phosphorous showed a significant positive correlation (P < 0.05) with potassium at all stations, with iron at S-I and S-II and with organic carbon and nitrogen at S-III. On the other hand it showed significant negative correlation (P < 0.05) with electrical conductivity at all stations in 2010. During 2011, it showed a significant positive correlation (P < 0.05) with potassium, copper and iron at all stations, with organic carbon, nitrogen and zinc at S-I and S-III, with pH at S- II and a significant negative correlation (P < 0.05) with electrical conductivity at all stations (Tables.4.13 to 4.18).

4.3.5 POTASSIUM

The monthly variation and average potassium content of the sediment samples measured at S-I to S-III for the study period are presented in Tables 4.1 and 4.2; Fig.4.9 and 4.10. In 2010, the values ranged from 2.11 ppm in January

to 17.7 ppm in July at S-I, from 3.67 ppm in January to 17.0 ppm in August at S-II and from 1.5 ppm in March to 21.6 ppm in July at S-III. The maximum monthly average potassium was recorded in S-II with 8.35±3.76 ppm against the minimum of 6.9±4.07 ppm in S-I. In 2011, the values ranged from 1.89 ppm in April to 14.86 ppm in June at S-I, from 2.01 ppm in April to 13.5 ppm in June at S-II and from 1.98 ppm in April to 15.9 ppm in July at S-III. The maximum monthly average potassium of 7.13±4.2 ppm was recorded in S-III and it was minimum (5.90 ±3.7 ppm) in S-I.

In the selected sampling stations (S-I to S-III) potassium content showed seasonal variations and are shown in Table 4.7. In the first year, during non monsoon season the minimum potassium content of 3.07±1.14 ppm was recorded in S-III against the maximum of 5.53±1.46 ppm in S-II. In the second year, S-I registered minimum potassium of 2.58±0.70 ppm and it was maximum (3.50 ±1.24 ppm) in S-III. In 2010, during southwest monsoon season the minimum potassium of 10.75±4.90 ppm was recorded in S-I against the maximum of 11.65±6.90 ppm in S-III. In the same season during 2011, the minimum value noticed was 8.89±4.70ppm in S-I and the maximum was 10.68±5.11 ppm in S-III. The northeast monsoon period registered minimum potassium of 5.87±1.44 ppm in S-I and the maximum of 8.33±1.60 ppm in S-III in 2010. In the second year, the minimum potassium recorded was 6.26±1.31 ppm in S-I and the maximum was (8.24 ±2.64) ppm in S-II.

Statistical analysis by two-way ANOVA (Table4.7.a) for the data on sediment potassium as a function of sampling stations and seasons revealed that

the variation between stations was not statistically significant during 2010 and 2011(F = 1.56 and 5.17; P > 0.05). But the variation in the potassium level between seasons was more significant in both the years of study period (F = 37.95 and 121.32; P < 0.01 and < 0.001).

Potassium exhibited a significant positive correlation (P < 0.05) with phosphorous and iron at all stations, with organic carbon, nitrogen and zinc at S-I, and with pH at S-III. It showed significant negative correlation (P < 0.05) with electrical conductivity at S-II and S-III. In 2011, potassium showed a significant positive correlation (P < 0.05) with phosphorous and zinc at all stations, with nitrogen, organic carbon and iron at S-I, with copper at S-III and a significant negative correlation (P < 0.05) with electrical conductivity at S-I and S-II (Tables 4.13 to 4.18).

4.3.6. ORGANIC CARBON

The monthly fluctuation and average sediment organic carbon recorded in the sampling stations during 2010 and 2011 are shown in Tables 4.1 and 4.2; Fig.4.11 and 4.12. During 2010, the minimum values recorded were: 0.07% in March at S-I, 0.10% in March at S-II and 0.12% in September at S-III. The maximum values recorded were: 0.21% in October at S-I, 0.29% in October at S-II and 0.27% in June at S-III. The monthly mean organic carbon content was maximum at S-III with 0.183±0.04% and minimum at S-I with 0.137±0.04%. In 2011, organic carbon content ranged from 0.072% in January to 0.22% in June, from 0.08% in March to 0.28% in July and from 0.09% in February to 0.26% in October at S-I, S-II and S-III respectively. The monthly average organic carbon

content recorded was maximum (0.177± 0.05%) at S-II and minimum at S-I with 0.138±0.04%.

The seasonal variations in organic carbon content in the sampling stations during the study period are presented in Table 4.8. In the non monsoon period during the first year (2010), the minimum organic carbon content recorded was 0.105±0.03% in S-I and the maximum was 0.165±0.03% in S-III. In the second year (2011), minimum organic carbon was 0.109±0.03% in S-I and the maximum was 0.158±0.06% in S-III. In 2010, during the southwest monsoon period the minimum organic carbon noticed was 0.15±0.02% in S-I against the maximum of 0.197±0.05% in S-III. In 2011, the minimum organic carbon registered was 0.155±0.02% in S-I against the maximum of 0.20±0.06% in S-II. During the northeast monsoon period of 2010, the minimum value registered was 0.155±0.05% in S-I and the maximum of 0.202±0.06% was noticed in S-II. In the same season during 2011, minimum organic carbon recorded was 0.15±0.02% in S-I and the maximum (0.198±0.04) was noticed in S-III.

Two-way ANOVA test (Table 4.8.a) revealed that the variations in sediment organic carbon between stations and seasons were statistically significant (F = 15.59 and 8.62; $P < 0.05$, F = 11.56 and 7.34; $P < 0.05$) during 2010 and 2011.

Organic carbon showed a significant positive correlation ($P < 0.05$) with nitrogen at all stations, with zinc at S-I and S-III, manganese at S-I and S-II and with potassium at S-I and phosphorous at S-III during 2010. In the year 2011, it significantly ($P < 0.05$) correlated positively with nitrogen and zinc at all stations,

with phosphorous at S-I and S-III, with potassium and iron at S-I and it showed a significant negative correlation (P < 0.05) with electrical conductivity at S-III (Tables.4.13 to 4.18).

4.3.7 COPPER

The monthly fluctuations and average copper content noticed in the sampling stations are depicted in Tables 4.1 and 4.2; Fig.4.13 and 4.14. The values recorded in 2010 ranged from 0.39 ppm in June to 1.42 ppm in August, from 0.51 ppm in October to 1.548 ppm in August and from 0.43 ppm in September to 1.668 ppm in August at stations I, II and III respectively. The monthly average value recorded was maximum with 0.80±0.35 ppm at S-II and minimum with 0.66 ±0.31 ppm at S-I. In 2011, the values fluctuated from 0.42 ppm in March to 1.625 ppm in August at S-I, from 0.52 ppm in April to 1.81 ppm in October at S-II and from 0.69 ppm in March to 1.55 ppm in November at S-III. The monthly mean value recorded in sampling stations was maximum (1.06±0.39 ppm) at S-II and minimum (0.804±0.34 ppm) at S-I.

The seasonal variation in copper was also computed and presented in Table 4.9. In 2010, during the non monsoon period, the minimum value noticed was 0.465±0.01 ppm at S-I; whereas the maximum value of 0.677±0.11 ppm was registered at S-II. During southwest monsoon season the minimum value recorded was 0.737±0.46 ppm at S-I and it was maximum (0.901±0.52 ppm) in S-III. In northeast monsoon season, the minimum value noticed was 0.781±0.27 ppm at S-I and the maximum (0.873±0.45 ppm) was at S-III. In 2011, during the non monsoon period, the minimum copper content registered was 0.58±0.22 ppm

at S-I and the maximum (0.87±0.33 ppm) was noticed at S-II. During the southwest monsoon season, the minimum value noticed was 0.86±0.51ppm in S-I and the maximum (1.05±0.29 ppm) was registered at S-III. In the northeast monsoon period, the minimum value noticed was 0.98±0.10 ppm at S-I and it was maximum (1.39 ±0.30 ppm) in S-II.

The two-way ANOVA (Table.4.9.a) revealed that the variation in sediment copper between stations was statistically not significant (F = 5.424 and 4.26; P > 0.05) during the study period. But the variation in sediment copper between seasons was statistically significant (F = 24.76 and 13.72; P < 0.01 and P < 0.05) during 2010 and 2011.

Copper showed a significant positive correlation (P < 0.05), with pH at S-II and S-III during 2010. In the year 2011, copper showed a significant positive correlation (P < 0.05) with phosphorous at all stations, with iron at S-I and S-III and with pH at S-II and S-III (Tables.4.13 to 4.18).

4.3.8 ZINC

The monthly fluctuation and mean zinc content in the sampling stations are presented in Tables 4.1and 4.2; Fig.4.15 and 4.16. In 2010, at S-I, the zinc content varied from a minimum of 0.6 ppm to a maximum of 1.36 ppm in March and October respectively. In S-II, the zinc ranged from a minimum of 0.69 ppm in April to a maximum of 1.51 ppm in October and in S-III, it varied from 0.80 ppm in August to 1.32 ppm in November. The maximum monthly average value was recorded in S-II with 1.054±0.26 ppm and it was minimum (0.88 ± 0.24 ppm) in S-I. During 2011, in S-I, the zinc fluctuated with a minimum of 0.25 ppm

in March to a maximum of 1.35 ppm in June. In S-II, the zinc ranged from a minimum of 0.5 ppm in March to a maximum of 2.31 ppm in July and in S-III, it varied from 0.20 ppm in February to 1.9 ppm in June. The maximum monthly average zinc was recorded in S-II with 1.141±0.47ppm against the minimum of 0.71±0.38 ppm in S-I.

Table 4.10 shows seasonal fluctuations in the zinc content during the study period. In 2010, during non monsoon period a minimum zinc content of 0.679±0.09 ppm was recorded in S-I and a maximum of 0.905±0.16 ppm in S-II. The southwest monsoon period showed a minimum of 0.89±0.23 ppm in S-I and a maximum of 1.02±0.17 ppm in S-III. During the northeast monsoon period, the zinc content recorded was 1.03±0.30 ppm in S-III and 1.26±0.32 ppm in S-II. In 2011, the non monsoon period registered the minimum zinc content of 0.335±0.17 ppm in S-I against the maximum of 0.785±0.28 ppm in S-II. During the southwest monsoon period, the minimum zinc content was noticed in S-I with 0.902±0.45 ppm and it was maximum (1.165±0.60 ppm) in S-III. The northeast monsoon period showed a minimum of 0.895±0.15 ppm in S-I and the maximum of 1.137 ±0.01 ppm in S-II.

Two-way ANOVA test (Table 4.10.a) revealed that in 2010 the variation in sediment zinc level between stations was not significant (F = 4.58; P > 0.05); whereas, in 2011 it was statistically significant (F = 16.47; P < 0.05). But the variation in sediment zinc level was statistically significant between seasons (F = 14.94 and 37.94; P < 0.05 and 0.01) during the study period.

In 2010, zinc showed a significant positive correlation ($P < 0.05$) with organic carbon, nitrogen and manganese at S-I and S-III and with potassium, phosphorous and iron at S-I but it showed a significant negative correlation ($P < 0.05$) with electrical conductivity at S-I. In 2011, a significant positive correlation ($P < 0.05$) was observed with potassium, phosphorus, organic carbon and nitrogen at all stations and it showed a significant negative correlation ($P < 0.05$) with electrical conductivity at S-I and S-II (Tables.4.13 to 4.18).

4.3.9 MANGANESE

The results recorded for the monthly fluctuations and average sediment manganese content at the sampling stations is depicted in Tables 4.1 and 4.2; Fig.4.17 and 4.18. In 2010, the manganese content varied from 0.72 ppm in January to 2.1 ppm in October at S-I. In S-II it showed a range of 0.5 ppm in February to 2.5 ppm in October and in S-III, it varied from 0.4 ppm in February to 2.35 ppm in October. The maximum monthly average value was recorded in S-II with 1.42±0.56 ppm and a minimum of 1.22 ±0.35 ppm in S-I. In 2011, the manganese content varied from 0.62 ppm in August to 2.4 ppm in November at S-I, from 1.18 ppm in September to 3.82 ppm in October at S-II and from 0.72 ppm in August to 2.617 ppm in October at S-III. The monthly average manganese value showed a variation from 2.02±0.77 ppm at S-II to 1.27±0.47 ppm at S-I.

Seasonal variations in sediment manganese noticed at the sampling stations are provided in Table 4.11. In 2010, the non monsoon period showed minimum manganese of 0.90±0.56 ppm in S-III and a maximum of 1.1±0.66 ppm in S-II. The southwest monsoon season recorded a minimum of 1.2±0.13 ppm in

S-I and a maximum of 1.38±0.20 ppm in S-III. During the northeast monsoon period, minimum manganese of 1.45±0.46 ppm was recorded in S-I and the maximum of 1.9±0.48 ppm in S-II. In 2011, non monsoon period showed a minimum content of 1.34±0.39 ppm in S-I and a maximum of 2.19±0.24 ppm in S-II. During southwest monsoon, the minimum value was 1.0±0.29 ppm in S-I and the maximum was 1.45±0.44 ppm in S-II. During the northeast monsoon period minimum manganese noticed was 1.49±0.66 ppm in S-I and it was maximum (2.44 ±1.10 ppm) in S-II.

The two-way ANOVA test (Table 4.11.a.) revealed that the variation in sediment manganese between stations was not statistically significant during 2010 (F = 1.665; P > 0.05); whereas it was more significant during 2011(F = 19.42; P > 0.01). The variation in the manganese level between seasons was statistically significant in both the years of study period (F = 18.66 and 16.93; P < 0.01 and <0.05). Manganese was significantly correlated (P < 0.05) positively with organic carbon and nitrogen at SI and S-II and with zinc at S-I and S-III during 2010 (Tables.4.13 to 4.18).

4.3.10 IRON

The monthly fluctuation and average sediment iron content recorded at the sampling stations during 2010 and 2011 are shown in Tables 4.1 and 4.2; Fig.4.19 and 4.20. During 2010, in S- I, the iron content varied from 5.582 ppm in May to 25.32 ppm in August. In S - II, it showed a range of 9.68 ppm in February to a maximum of 28.6 ppm in September and in S - III, it varied from 6.714 ppm in March to 28.06 ppm in July. The maximum monthly average value

was recorded in S-II with 17.45±5.96 ppm and a minimum of 12.63 ±6.8 ppm was recorded in S-I. In 2011, the iron content in sediment varied from 4.8 ppm in March to 22.42 ppm in November at S-I, from 9.82 ppm in May to 18.44 ppm in November at S-II and from 7.89 ppm in February to 18.99 ppm in November at S-III. The monthly average iron content showed a variation from 13.53±2.55 ppm at S-II to 10.52±4.93 ppm at S-I.

Table 4.12 shows the seasonal variations in sediment iron in the sampling stations. In 2010, during non monsoon period a minimum iron content of 7.38 ±2.3 ppm was recorded in S-I against the maximum of 13.15 ±2.5 ppm in S-II. The southwest monsoon period showed a minimum of 17.01 ± 8.8 ppm in S-I and it was maximum (19.24± 6.4 ppm) in S-II. In northeast monsoon period, the minimum iron content (13.48 ± 4.8 ppm) recorded in S-I and it was maximum (19.98 ± 6.6 ppm) in S-II.   In 2011, the non monsoon period showed minimum value of 6.38 ±1.5 ppm in S-I and a maximum of 12.53±1.7 ppm in S-II. During the southwest monsoon period, the minimum iron content was noticed in S-I with 10.87±3.4 ppm and the maximum of 13.33±2.4 ppm in S-II. The northeast monsoon period showed a minimum of 14.3±5.75 ppm in S-I and the maximum of 15.61 ±2.74 ppm in S-III.

The two-way ANOVA test (Table 4.12.a) revealed that the variation in sediment iron content between stations was statistically significant during 2010 (F = 13.22; P < 0.05); whereas, it was not significant during 2011(F = 2.77; P > 0.05). The variation in the iron content between seasons was statistically

significant in both the years of study period (F = 40.0 and 8.925; P < 0.01 and < 0.05).

Iron showed a significant positive correlation (P < 0.05) with potassium at all stations, with phosphorous at S-I and S-II and with zinc at S-I. It showed a significant negative correlation (P < 0.05) with electrical conductivity at all stations in 2010. During 2011, it showed a significant positive correlation (P < 0.05) with phosphorous at all stations, with potassium, organic carbon, nitrogen and zinc at S-I, with copper at S-I and S-III and with pH at S-III. On the other hand, it showed a significant negative correlation (P < 0.05) with electrical conductivity at S-II and S-III (Tables 4.13 to 4.18).

4.4. DISCUSSION

Estuaries are precious and productive coastal sites, subject to high demand for a variety of uses. Disposal of sewage and pollutants often resulted in degradation of the environmental quality. The scavenging by suspended particles results in large concentrations of pollutants being retained in estuarine sediments (Juracic and Prohic, 1986). Solids entering the estuary are either products of weathering or are related to human intervention. The characteristic features of an individual river basin such as its climate, vegetation, morphology and the mineral composition of its soils and rocks, constitute the background conditions which determine the chemical composition and quantities of material carried by the river and deposited in its estuary. The heavy metals generally enter the aquatic environment through atmospheric deposition, erosion of geological matrix or due to anthropogenic activities caused by industrial effluents, domestic sewage and mining wastes (Solai *et al*., 2010). Sediment accumulation, which badly influences almost all the economic activities in the backwater, is an important form of externality caused both by natural processes and human actions.

The major factors governing the pH of soil includes the concentration of reduced metals like iron, manganese as well as carbonates, carbonic acid and humic acid (Patrick and Mikkelsen, 1974). The sediment pH showed wide fluctuations during the study period. Low pH values were recorded in S-II and S-III compared to S-I and it may be due to the increased rate of decomposition in the organic matter and mixing of retting effluent and sewage accumulation. Saha (1985) reported that low pH values were due to the increased rate of

decomposition in the organic matter and conversion of released carbon dioxide into carbonic acid. In Adyar estuary the sediment was found to be acidic in reaction due to the influence of sewage accumulation (Joseph *et al*., 1992). Vishnu (2005) noticed an acidic sediment pH in Ashtamudi estuary. According to Unnithan *et al.* (2001) low pH could be due to exposure of relatively higher acidic subsurface basin soil consequent on monsoon turbulence and bottom currents. Lowering of pH can be due to release of biogenic carbon dioxide by bacterial decomposition of organic matter (Berner, 1971). Davies and Abowei, (2009) observed low pH values in the brackish water environment of the Nigeria delta due to sulphur compounds like hydrogen sulphide. In the present study high pH values were reported in northeast and southwest monsoon season but low pH values were recorded in non monsoon season during 2010. In 2011 high values were reported in northeast monsoon season and low values during non monsoon and southwest monsoon. Selvamohan (2006) observed maximum pH during southwest monsoon season. Umayorubhagan *et al*. (1998) also reported an increase in pH during rainy season and decrease during non monsoon period. The highest sediment mean pH was noted during monsoon season and the lowest, during post monsoon (Soumya *et al*., 2011). Vasantha (2009) noticed higher pH values during the pre-monsoon months and lower values during the monsoon months. Fluctuations in pH values during different seasons of the year is attributed to factors like removal of CO_2 by photosynthesis through bicarbonate degradation, dilution of seawater by freshwater influx, reduction of salinity and temperature and decomposition of organic matter (Upadhyay, 1988 and Rajasegar, 2003). The relatively low value of pH during the dry season could be

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as a result of the oxidation of FeS to H_2SO_4 (Ramanathan, 1997). pH showed both positive and negative correlation with other tested sediment quality parameters at most of the sampling stations during the study period.

Electrical conductivity of the wet soil depends on several parameters such as electrical conductivity of water present between the particles in the soil and percentage of pore water in the sediment (Keller and Frischeknecht, 1996). In the present study high values of EC were recorded during non monsoon period. Singh and Sharma (1986) reported high EC during non monsoon months due to increase in ambient temperature. During monsoon the EC value decreases as the rain water dilutes the salt content in the estuarine environment. The continuous decrease of electrical conductivity from sea mouth towards the river mouth is an indication of calm hydrodynamic conditions prevailing in the estuary, as the sediments have not undergone sufficient mixing (Jeena Pearl, 2010). Ansa and Francis (2007) reported low pH sediment had the highest conductivity and high pH sediment showed low conductivity. In the present study electrical conductivity showed a significant negative correlation ($P < 0.05$) with pH at all stations.

Low values of organic matter in sediment may be the result of marine sedimentation and mixing processes at the sediment water interface where rates of delivery and degradation by microbial-mediated processes can be high (Dikou Angela and Triantaphyllou Nikos, 2008). The organic nitrogenous compounds produced from the degradation of organic matter gets adsorbed into sediments depending upon the temperature, electrical conductivity of the interstitial water,

the concentration of organic matter and the porosity of sediments (Rosenfield, 1979). In the present study, higher nitrogen content was noticed during monsoon and low concentration during non monsoon. Higher nitrogen content during the monsoon season could be attributed to the down loading of this nutrient by floodwater and also by the deposition of agricultural runoff (Prabha Devi, 1986). Low values of sediment nitrogen during pre-monsoon were attributed to the combined effects of biological utilization and desorption from suspended particulates (Nasnolkar *et al*., 1996). Vasantha (2009) noticed maximum sediment nitrogen during monsoon when the temperature, pH and organic carbon were low and minimum nitrogen during pre-monsoon**.** (Saravanakumar *et al*., 2008) recorded lower value of total nitrogen during monsoon season may be ascribed to low level of organic matter. In Swartkops estuary in Africa, Dye (1978) observed high nitrogen content in finer substrate and suggested that it was probably due to trapping of detritus by finer particles, resulting in an increase in bacterial population. In the present study total organic carbon, total nitrogen and total phosphorus values were lower than the values recorded by many workers from various environments.

Phosphorus is regarded as an important factor in the determination of biological productivity of water. The concentration and distribution of phosphorus in the sediment are related to the amount of available organic matter in the sediments (Mathevan Pillai, 1994). Organic phosphorous in the sediment gets bound with the shells and bones of invertebrate animals and when the shell breaks the phosphorus is released into the sediments. In the present study, high phosphorous concentration was recorded in S-III compared to S-I and S-II it may

be due to domestic sewage and agricultural effluents. Very low concentration of phosphorous in S-I may be due to the sandy nature of the soil. Rajagopal and Reddy (1984) observed high phosphate in clayey slit type sediments in Mandovi estuary. High values of phosphorous might have been promoted by the deposition of inorganic phosphate due to runoff from the land during monsoon, domestic sewage and agricultural effluents (Eyre, 1993). Increased application of fertilizers, use of detergents and domestic sewage play a great role in contributing to the heavy loading of phosphorus in sediments (Golterman, 1975). In the present study, seasonal variation of the phosphorous concentration showed maximum values during southwest monsoon in 2010 and northeast monsoon in 2011 but minimum values were recorded during non monsoon period. Prabha Devi (1986) observed an increase in Phosphorous content of the sediment during the monsoon in Coleroon estuary. Saha (1985) reported that maximum value during rainy season and minimum value during summer season may be due to oxygen deficiency in water during which phosphorus is released in the water from sediments. Similar observations were also made by Umayorubhagon *et al*. (1998); Prema (2002) and Selvamohan (2006). The observed high phosphorous content in the present investigation may be due to the entrapment of the river derived phosphorous through assimilation and subsequent deposition in sediments and the lower concentration of phosphorous during non monsoon may be due to biological utilitsation. The capacity of sediment to retain or release phosphorus is one of the important factors, which influence the concentration of inorganic/organic phosphorus in the overlying waters. Higher values of phosphates recorded during the rainy season may be due to dead organic matter

from the top layer and low values during the dry season may be related to removal of top layer of sediments by heavy floods (Saravanakumar *et al*., 2008; Jyothibabu *et al.,* 2006; Tukura *et al*., 2012). In the present study, both positive and negative relationship was obtained for the total phosphorous with other tested soil quality parameters. Similar type of observation was reported by Vinithkumar *et al*. (1999).

Potassium is a common rock-forming mineral and is associated with non-carbonate minerals in the coastal sediment. Biswas and Boruah (2000) reported that high value of potassium was due to heavy pollution load in Adyar River. In the present study also maximum potassium was reported at S-II and S-III which is polluted by retting effluents and also sewage and domestic wastes from nearby villages. Mohideen Askar Nawas (2009) reported that high values of potassium were due to the leaching of potassium through rain water from the surrounding coconut fields which contain potash in the form of fertilizer. Season wise pooled data showed maximum values during southwest monsoon and low values during non monsoon and northeast monsoon. The heavy river run off mainly causes the higher concentration of potassium during monsoon. Similar condition was noticed by Mishra *et al*. (1993) in Bahuda estuary; Shumilin *et al*. (2002) in Colorado River delta. The maximum values during the monsoon season were also observed by Umayorubhagan *et al*. (1998); Indrani (2003); Kumaraswamy (2005) and Vasantha (2009). Low values recorded during pre-monsoon period may probably be due to its utilization by biological activity and low fresh water flow (Seralathan and Seetaramaswamy, 1979). Sundararajan and Natesan (2010) recorded high potassium in post monsoon than pre-monsoon and monsoon. In the

present study potassium exhibited a significant positive correlation with phosphorous, organic carbon and nitrogen in selected sampling stations. Vinithkumar *et al.* (1999) reported a positive correlation between potassium with total nitrogen and organic carbon.

The relatively low percentage of organic carbon was recorded at S-I this may be due to constant flushing activity by tides along with the impact of waves, which removes the finer fraction of the sediments from the area. The sand bar at the estuarine mouth was opened following heavy rainfall and the sediment deposited in the bottom is flushed out into the sea along with the floodwater may be the reason for low organic carbon in S-I. Organic carbon increases with increasing finer fraction and decreases with the increasing coarse fraction in sediments (Sugirtha Kumar and Edward Patterson, 2009) and Sunil Kumar (1996). High percentage of organic carbon was associated with the finer sediments (Purandara and Dora, 1987). The low content of organic carbon noted in the present study may be due to the sandy sediment. De la Lanza *et al.* (2011) also reported low organic carbon content in sandy sediments of a tropical coastal lagoon complex. Friedman (1978) stated that wave action and tidal currents are enough to produce the development of sandy sediment in intertidal zones. In the present study high values were reported in the month of June and October it may be due to the influx of land run off containing a more amount of terrigenous organic matter. Organic carbon content was relatively more at S-II and S-III; this may be due to the discharge of large amount of humus brought to this region along with the sewage inputs from the nearby villages. Seasonally pooled data showed more organic carbon during monsoon and low concentration during non

monsoon. Sarala Devi (1989) recorded high valued of organic carbon during monsoon months and low during post monsoon months in Cochin backwaters. The high organic carbon in the monsoon period may be due to land runoff, sewage discharges through the river and the plant and animal matter brought through the runoff (Lakshmi *et al*., 2000). Kumaraswamy (2005) also reported high organic carbon during monsoon season in Thengapattinam estuary. Nair *et al*., (1983b) observed a pre-monsoon increase in organic carbon in the sediments of Ashtamudi estuary. Vasantha (2009) and Murugan and Ayyakkannu (1991) observed highest organic carbon during   pre-monsoon and the lowest during monsoon. Dora and Borreswara Rao (1975) recorded comparatively higher concentration of organic matter in the pre-monsoon sediments than in the postmonsoon season, The high organic carbon content in pre-monsoon would have resulted from the decomposition of organic matter deposited in sediment (Rajasegar *et al*., 2002). The lower value during monsoon might be due to incessant stirring up of the sediments releasing the organic carbon from the sediment to the water column and also the sediment was mainly composed of sand brought out by incessant flow of waters during monsoon season (Bragadeeswaran *et al*., 2007). The high organic carbon content in the sediments of the riverine part of the creek is due to fine nature of the sediments and high rate of sedimentation (Sundararajan and Natesan, 2010). In the present study organic carbon content was found to be low at all stations. The irregularity in the behavior of the organic carbon may be due to biological utilization of carbonaceous detritus matter and sandy nature of the sediments. In the present study organic carbon showed positive correlation with total nitrogen at all

stations. Nasnolkar *et al.* (1996), Sukumaran (2002), Kumaraswamy (2005) and Mohideen Askar Nawas (2009) have reported such a significant positive correlation for nitrogen with organic carbon in Mandovi, Manakudy, Thengapatanam and Rajakkamangalam estuaries respectively.

Sediments can be a sink or a source for trace metals in water.Trace metals need not necessarily be definitely fixed in the sediment, and recycling can occur by biological, chemical and physical processes (Carignan and Nriagu, 1985). The role of organic matter and sediment grain size in relation to the accumulation of heavy metal to the sediment has often been emphasized (Davies *et al.,* 1991). Increases in heavy metal concentrations tend to be associated with finer grained sediments and higher heavy metal concentrations in the estuary are found at the sites, where finer sediments occur (Binning and Baird, 2001). Heavy metal ions accumulate in estuarine sediments because of the deposition of metal-enriched allochthonous particles or the adsorption of dissolved heavy-metal ions from the water column (Rodrigo, 1989). Organic matter acts as a metal carrier and plays an important role in the metal distribution patterns (Lin and Chen, 1998 and De Groot *et al*., 1982). Pekey (2006) and Shriadah (1999) stated that most contaminants are transported as fine-grained suspended matter which has large surface area. Concentration of metals in sediments depends on several factors such as local conditions, particle size and organic matter content (Aston and Chester, 1976). Fine grained sediments (clays, clayey silts) are characterized by higher metal concentration in sediment (Devavarma *et al*., 1993). Zhou *et al*. (2004) in the Pearl river estuary found that the concentration of Cu and Zn were high due to the higher degree of industrialization. High concentrations of heavy

metals are due to the discharge of untreated effluents from different industries (Anju kumar *et al*., 2011). Magnitude of difference in metal concentrations observed between dry season and wet season cannot be explained in response to temporal condition (Mukherjee and Kumar, 2012). Trace metal enrichments are mainly due to anthropogenic contribution of industrial, domestic and agricultural effluents, whose effect is enhanced by settling of metals due to organic flocculation and inorganic precipitation associated with salinity changes (Martin *et al*., 2012).

In the present study copper content was high during monsoon season and low during non monsoon season. High concentrations of copper in the sediments during the monsoon period may be due to downstream transport along with the monsoonal discharge. Senthilnathan and Balasubramanian (1999) also reported higher concentration of copper in sediments from Pondicherry harbor during monsoon and lower in summer. This was attributed to land runoff and influx of metal rich water. Similarly, higher concentrations of copper in sediments were reported from Godavari estuary during monsoon season (Srinivas, 1998). Concentration of copper decreases from the pre-monsoon to the monsoon and again increases during the post-monsoon (Alagarsamy, 2006). Phytoplankton activity can cause seasonal variation in Cu as this metal is an essential one for phytoplankton (Govidasamy and Azariah, 1999). Anitha Mary *et al*. (2012) observed higher levels of copper in estuarine region whereas lower levels at the mouth of the estuary and freshwater zones.

Zinc is an essential trace metal and is an important component for plants and human. In 2010, zinc content was more in northeast monsoon period but in 2011 high concentration of zinc was recorded during southwest monsoon period. The high values recorded during monsoon may be due to the effect of increased inputs of land derived metals. Similar observations were made by Srinivas (1998) in Godavari estuarine sediments, Satheeshkumar and Senthilkumar (2011) in Pondicheery Mangroves and Chakraborty *et al*., (2009) in the estuarine stretch of West Bengal. Zinc can enter the aquatic environment from a number of sources including industrial discharges, sewage effluent and runoff (Boxall *et al*., 2000). In the present study high zinc content was reported in S-II it may be due to the mixing of domestic and retting effluents. Paul and Pillai, (1983) and Shibu *et al*., (1990) noticed anthropogenic source contributing to the enrichment of zinc in the sediment of Cochin backwater.

In the present study high Mn content is observed during monsoon season and low during nonmonsoon period. Similar trend was also observed by Srinivas (1998), Ganesan and Kannan, (1995). The high Mn concentrations observed in sediment are related to high levels of manganese in the surrounding ore bearing landmass (Zingde *et al*., 1976). In the present study high values were recorded in riverine side and low value near the bar mouth, this may be due to the mixing of domestic waste and sewage from the nearby villages. But Sundararajan and Natesan (2010) reported high values near the mouth of the estuary and less at the riverine end.

The removal of dissolved river borne iron by coagulation in estuaries is more common (Holliday and Liss, 1976 and Boyle *et al.,* 1977). In the present study, during 2010 high iron content is recorded in southwest monsoon season in S-I and S-III but in S-II it is high in northeast monsoon. In 2011, iron content was high during northeast monsoon and low during non monsoon. Higher concentration of iron recorded during monsoon may be due to the increased land off. Senthilnathan and Balasubramanian (1997) recorded high values of iron during monsoon due to increased particulate matter along with suspended sediment load. Ganesan and Kannan (1995) had reported high content of iron during monsoon and post-monsoon in Tuticorin coast, which is attributed to increasing land runoffs. Srinivas (1998) while studying Godavari estuarine sediments observed higher concentrations during monsoon seasons. Inengite *et al*. (2010) also noticed more iron content in sediments of Kolo Creek during rainy season. Martin *et al*. (2012) recorded more or less similar concentrations of Fe during the monsoon and pre-monsoon period.