

3. PHYSICOCHEMICAL PARAMETERS OF WATER

3.1. INTRODUCTION

India has a coastline of over 8000 km long infringed with several rivers draining a total catchment of $3.02 \times 10^6 \text{ km}^2$ and their estuaries have a water-spread area of $2.7 \times 10^4 \text{ km}^2$. There are 14 major, 44 medium and 162 minor rivers which together discharge $1.56 \times 10^{12} \text{ m}^3$ runoff every year greatly influencing ecology of their estuaries and coastal areas to which they drain (Kumaraswamy, 2005). Major portion of the pollutants that are introduced into the environment are distributed in water, sediment and biota. As urban and industrial development continues the rate of unintentional release of contaminants to surface and subsurface waters are also increased. As a result, there is a need for effective assessment of such environment parameters (Winter, 2000). Areas around streams, rivers, lakes and coastal environments represent zones of interaction and transition between the two systems where dissolved constituents such as pollutants can be diluted, exchanged, transformed or destroyed.

Estuaries receive significant anthropogenic inputs from both point and non-point upstream sources and from metropolitan areas, tourism and industries located along the estuarine edges. Rivers play a major role in assimilation or carrying of municipal and industrial wastewater and runoff from agricultural land. For confirming the good quality of water resources, large number of

physicochemical parameters, extent and source of any pollution load must be known for which monitoring of physicochemical parameters and pollutants is essential (Reddi *et al.*, 1993). Assessment of water resource quality from any region is an important aspect for the developmental activities of the region, because the rivers, lakes and reservoirs are used for water supply to domestic, industrial, agricultural and fish culture (Jakher and Rawat, 2003). Rivers play a crucial role in the delivery of nutrients to the ocean, making coastal waters particularly prone to eutrophication, which may cause harmful algal blooms and hypoxia, disrupting coastal ecosystems (Rabalais *et al.*, 2002; Galloway *et al.*, 2004; Howarth and Marino, 2006; Smith *et al.*, 2006). An over-supply of nutrients is documented extensively washed from the soil into rivers and estuaries (Conley *et al.*, 1993; Paerl, 1997; Howarth, 1998).

A large number of physical and chemical processes take place in estuaries when river water mixes with seawater, which may influence the water quality. The quality of surface water is a very sensitive issue. Physical, chemical and biological features of the estuary are adapted to a seasonal rhythm induced by the annual cycle of the monsoon (Qasim and Gupta, 1981). The oxygen dissolved in water is a very important parameter in water analysis as it serves as an indicator of the physical, chemical and biological activities of the water body. The diffusion of oxygen from the air and photosynthetic activity are the two main sources of dissolved oxygen. Oxygen is considered to be the major limiting factor in water bodies with high concentration of organic materials. It is well known that the temperature and salinity affect the dissolution of oxygen (Vijayakumar *et al.*, 2000). Insufficient dissolved oxygen in the water column causes anaerobic

decomposition of any organic material present, which tends to cause the formation of noxious gases such as hydrogen sulphide and development of CO₂ and methane in the sediments, which bubble to the surface or tend to float on the settled sludge as mat, which are decomposed of various organic materials (Karunagaran, 1990). Evaporation and rainfall may have considerable influence on the salinity distribution in estuaries, in particular in semiarid and arid zones (Savenije, 1988).

Substantial river discharges and relatively shallow near shore waters often result in large fluctuations and strong spatial gradients in salinity. In most of the estuaries reduced salinity is associated with finer substrates and this finer substrate easily reduces salinity from estuaries. Salinity of estuaries usually increases from a freshwater source such as river, although evaporation sometimes causes the salinity at the head of the estuary to exceed seawater. The vertical salinity structure and the nature of salinity variation along the estuary are the features of the salinity structure of coastal waterways (Santoro *et al.*, 2008).

Determination of dissolved inorganic nutrients (such as nitrogen, phosphorus and silicon) has been used in the evaluation of eutrophication in aquatic ecosystems, since these substances are closely related to the system's degree of pollution (O'Donohue and Denisson, 1997). The nutrient loading by the rivers influences the biotic activity in estuaries and coastal seas and may be an important indicator of changes in the condition of such waters (Sawidis and Tsekos, 2004). Water quality is important to assess the health of a watershed and to make necessary management decisions to control current and future pollution

of receiving water bodies (Khadam and Kaluarachchi, 2006; Behbahaninia *et al.*, 2009). It is well understood that concentrations of biologically available nitrogen and phosphorus play a key role in determining the ecological status of aquatic systems (Jarvie *et al.*, 1998). An excess of these nutrients can lead to problems such as toxic algal blooms, loss of oxygen, fish kills, loss of biodiversity, loss of aquatic plant beds and coral reefs. Nutrient enrichment seriously degrades aquatic ecosystems and impairs the use of water for drinking, industry, agriculture, recreation and other purposes (Carpenter *et al.*, 1998). Many tropical estuaries of the world have been recently the subject of hydrological studies due to the large benefits they provide to the coastal zone. However, the existing data are still insufficient to understand the physical and hydrological processes responsible for their sustainability.

Physicochemical parameters of Uppanar backwater were studied by Murugan and Ayyakkannu (1991); Mathavan Pillai (1994); Karthikeyan *et al.* (2004); Rajaram *et al.* (2005) and Soundarapandian *et al.* (2009). The physicochemical characteristics of Rushikulya estuary were studied by Gouda and Panigrahy (1992, 1993 and 1995); Tripathy *et al.* (1990) and Deepak and Sahu (1999). The hydrology of Hoogly estuary was studied by Ghosh and Basu (1968); Ghosh and Choudhury (1989); Ghatak and Konar (1994) and Sadhuram *et al.* (2005).

The physicochemical characteristics of Goutami- Godavari were studied in detail by Raman *et al.* (1989); Sastry and Chandramohan (1990) and Padmavathi and Satyanarayana (1999). The physicochemical characteristics of

Coleroon estuary were studied in detail by Jagadeesan and Ayyakannu (1992). The physicochemical parameters of Periyar estuary were studied by Remani *et al.* (1980); Sankaranarayanan *et al.* (1986); Lakshmanan *et al.* (1987) and Sarala Devi *et al.* (1989).

The hydrobiology of Cochin backwaters and its branches were studied by Qasim and Gopinath (1969); Sankaranarayanan and Qasim (1969); Devassy and Gopinath (1970); Shynamma and Balakrishnan (1973); Vijayan *et al.* (1976); Manikoth (1978); Lakshmanan *et al.* (1982); Nair *et al.* (1983 a, b, c and 1984); Nair and Azis (1987); Ramamirtham and Muthusamy (1986); Narayana Pillai (1993) and Menon *et al.* (2000). Jose Xavier *et al.* (2005) in Chaliyar river estuary in Kerala, Leena Grace (2006) in the Kadinamkulam backwater, Anila Kumary *et al.* (2007) in Adimalathura estuary, Mahesh Mohan and Omana (2007) in Vembanadu backwaters, Meera and Bijoy Nandan (2010) in Valanthakad backwater of Kerala and Narendra Babu *et al.* (2010) in Ashtamudi estuary.

Mandovi-Zuari estuarine system has been studied during different seasons by Das *et al.* (1972); Singbal (1973 and 1976); Goswami and Singbal (1974); Varma *et al.* (1975); De Souza (1977); Qasim and Sengupta (1981) and George *et al.* (1984). Asha and Diwakar (2007) studied hydrobiology of the inshore waters of Tuticorin. The physicochemical aspects of Vellar estuary were analysed by Krishnamurthy (1967b); Ramamoorthi and Venugopalan (1976); Ramadhas (1977); Sivakumar (1982); Chandran and Ramamoorthi (1984 a, b) and Shanthi *et al.* (1990).

Evangelina (1975) studied the physicochemical characteristics of estuary in the Ramanathapuram district. The ecological studies were carried out by Joseph *et al.* (1982) in the Adyar estuary. Vijayakumar (2000) studied the ecological parameters in the Mulki estuary. Vedamurthy (2000) studied the distribution pattern of particulate matter in the Nethravathi – Gurpur estuary; Rajesh *et al.* (2002) studied the ecology of Nethravathi estuary. Other ecological studies were done by Rajathy and Azariah (1996) and Padmini and Kavitha (2003) in the Ennore estuary, Sukumaran (2002); Taradevi (2002) and Jansi (2004) in Manakudy estuary, Prema (2000); Selvamohan (2006) and Mohideen Askar Nawas (2009) in the Rajakkalamangalam estuary. Estuarine characteristic of lower Krishna River was observed by Rajani kumari and Mrutyunjaya Rao *et al.* (2009). Physicochemical characteristics of Devi estuary was analyzed by Pradhan *et al.* (2009). Prasanna and Ranjan (2010) studied the physicochemical properties of water collected from Dhamra estuary. Seasonal variation of physicochemical characteristics of Point Calimere coastal waters was analysed by Damotharan *et al.* (2010).

Considering the information provided above, an attempt has been made to study the monthly and seasonal variation in physicochemical parameters of the water samples collected from the selected sampling stations of the experimental estuary.

3.2. MATERIALS AND METHODS

The present study was carried out over a period of two years (January 2010 – December 2011). Water samples were collected early in the morning in 100ml plastic containers in triplicate once in a month from the sampling stations. The collected samples were transported to the laboratory in plastic containers maintained at about 5°C and analyzed for their physicochemical parameters. For the estimation of dissolved oxygen, water samples were collected in brown Pyrex bottles (125 ml capacity) and fixed in sampling stations. The fixed samples were neatly labeled, covered with dark paper to avoid penetration of sunlight and brought to the laboratory for further analyses.

3.2.1. TEMPERATURE

Atmospheric and water temperature, accurate to the nearest 0.1 °C was recorded using a mercury thermometer. Atmosphere and surface water temperature of all the stations were recorded in the experimental stations itself.

3.2.2. HYDROGEN ION CONCENTRATION (pH)

The pH of the solution is a measure of its hydrogen ion activity .The term pH is the negative logarithm of hydrogen ion concentration.

$$\text{pH} = -\log [\text{H}^+]$$

The pH of water samples collected from the sampling stations was recorded by using a digital pH meter (LIH0).

3.2.3. SALINITY

The salinity of the water was measured by optical salinity Refractometer, New 100 (Thanka Sanjiro Co. Ltd., Japan).

3.2.4. DISSOLVED OXYGEN

Dissolved oxygen content of water samples was estimated by Winkler's method (APHA, 1985). The samples were fixed in the field itself by adding, 2ml of manganous sulphate and 2ml of alkaline iodide solution. The fixed samples were brought to the laboratory for further titration. The precipitate was then dissolved by adding 2ml of concentrated sulphuric acid. From this, 50 ml of sample was taken in a conical flask. A few drops of starch solutions were added to the conical flask as an indicator. This was titrated against 0.025 N sodium thiosulphate taken in the burette. The disappearance of blue colour was noted as the end point. The titration was repeated for each sample to get the concordant values. Then the dissolved oxygen present in the sample was calculated as follows:

$$\text{Dissolved oxygen (ml/l)} = \frac{\text{CD} \times \text{M} \times \text{E} \times 1000 \times 0.698 \times \text{Vt}}{\text{Vs}}$$

Where

$$\text{CD} = \frac{\text{Volume of the bottle}}{\text{Volume of bottle} - \text{Volume of reagent}}$$

- M = Normality of sodium thiosulphate (0.025 N)
- E = Equivalent weight of oxygen (8)
- 1000 = to express dissolved oxygen per litre
- 0.698 = To convert parts per million to ml of oxygen / litre
- V_t = Volume of titrant
- V_s = Volume of sample

3.2.5. CARBON DIOXIDE

The carbon dioxide content of water samples collected from the experimental stations was estimated by titrimetric method (APHA, 1985). Two drops of phenolphthalein indicator were added to 100 ml of the sample. The pink colour samples were titrated with hydrochloric acid and the colourless samples were titrated with 0.025 N sodium hydroxide. The amount of carbon dioxide present in the sample was calculated as shown below.

$$\text{Carbon dioxide (ppm)} = T \times 10$$

Where

T = Titre value

10 = Constant value

3.2.6. BIOLOGICAL OXYGEN DEMAND (BOD)

The BOD content in water samples was estimated by Winkler's method (APHA, 1985). About 250 ml of sample was taken in the BOD dark bottles. To this 1ml each of MnSO₄, CaCl₂, Phosphate buffer, Ferric chloride and Sodium

sulphite were added. The bottles were then kept in the BOD incubator at 20°C for five days. After the incubation period the samples were analysed for their oxygen content. From the difference between initial and final oxygen content the BOD was calculated.

$$\text{BOD (ml/l)} = \text{DO}_0 - \text{DO}_5$$

Where

DO_0 = Initial dissolved oxygen content

DO_5 = Final dissolved oxygen content

3.2.7. CARBONATE AND BICARBONATE

The carbonate and bicarbonate content of the water samples were estimated by phenolphthalein and mixed indicator titrimetric method (APHA, 1985). 100 ml of sample was taken. To this, 3 to 4 drops of phenolphthalein indicator were added and titrate against H_2SO_4 and the titre values were recorded. Then to the same sample 3 to 4 drops of mixed indicator were added and titrate against H_2SO_4 till the colour changed from blue to orange and then the titre value was recorded. From these titre values the amount of carbonate and bicarbonate were calculated as follows:

$$\text{Alkalinity due to CO}_2 = 2P \times 10 \text{ ppm}$$

$$\text{Alkalinity due to HCO}_3 = T - 2P$$

Where,

P = ml of acid used for titration with phenolphthalein.

T = ml of acid used for the total titration (phenolphthalein + mixed indicator).

3.2.8. ELECTRICAL CONDUCTIVITY

The conductivity of water samples collected from the experimental stations was measured by using a conductivity meter (Rao, 1993).

3.2.9. CALCIUM

The amount of calcium content present in the estuarine water was estimated by EDTA method of complexometric titration (APHA, 1985). For this 50 ml of sample was taken and to this 2ml of NaOH solution was added. Then a pinch of murexide indicator was added. It was titrated against EDTA until the pink colour changed to purple. Finally the amount of calcium present in the water was calculated as follows:

$$\text{Calcium (ppm)} = \frac{T \times 1000 \times 1.05}{V_s}$$

Where

T = Volume of titrant

V_s = Volume of sample

3.2.10. MAGNESIUM

The magnesium content of the water sample was estimated by EDTA method (APHA, 1985). To the 50 ml of sample, eriochrome black-T indicator was added and titrated against EDTA. From the titre value the amount of magnesium present in the sample was calculated as follows:

$$\text{Magnesium (ppm)} = T - C \times 0.244$$

Where,

T = Total hardness

C = Calcium hardness

3.2.11. SILICATE

The silicate content in the estuarine water sample was estimated by ammonium molybdate method (APHA, 1985). For this 50 ml of sample was taken. To this 1 ml of HCl acid and 2ml of ammonium molybdate solution were added. After ten minutes 1 to 5 ml of oxalic acid was added. The colour intensity was measured in a spectrophotometer at 410 nm. From this value the amount of silicate was calculated as given below.

$$\text{Silicate } (\mu\text{g/l}) = \frac{\text{Conc. of standard} \times \text{OD of unknown sample}}{\text{OD of known sample (Standard)}}$$

3.2.12. PHOSPHORUS

The inorganic phosphorus content of the water samples were estimated by stannous chloride method (APHA, 1985). 25 ml of water sample was taken. To this 1ml of ammonium molybdate solution and 3 drops of stannous chloride were added till the appearance of blue colour. The absorbance was recorded at 690 nm in a spectrophotometer. The amount of inorganic phosphorus was calculated as follows:

$$\text{Inorganic phosphorus } (\mu\text{g/l}) = \frac{\text{Con. of standard} \times \text{OD of unknown sample}}{\text{OD of known sample (Standard)}}$$

3.2.13. NITRITE

The nitrite content of water sample was estimated by sulphanilamide (spectrophotometric) method (APHA, 1985). 50 ml of sample was taken in clean conical flask. To this, 1 ml of sulphanilamide solution was added. After 3 minutes, 1 ml of n-(1-naphthyl) ethylenediamine dihydrochloride solution was added. The optical density of this mixture was measured at 543 nm in a spectrophotometer. From this value, the amount of nitrite present in the water was calculated as follows:

$$\text{Nitrite } (\mu\text{g/l}) = \frac{\text{Conc. of standard} \times \text{OD of unknown sample}}{\text{OD of known sample (standard)}}$$

3.2.14. NITRATE

Nitrate present in the water samples collected from the estuary was estimated by brucine sulphanilic acid method (APHA, 1985). 10 ml of sample was taken. To this 2 ml of NaCl solution was added and shaken well. Then 10 ml of sulphuric acid was slowly added followed by 0.5 ml brucine-sulphanilic acid, shaken well and again the mixture was placed in hot water bath for 20 minutes. The optical density was then measured at 543 nm in a spectrophotometer. From this recorded value the quantity of nitrate present in the water sample was calculated as shown below.

$$\text{Nitrate } (\mu\text{g/l}) = \frac{\text{Con. of standard} \times \text{OD of unknown sample}}{\text{OD of known sample (standard)}}$$

3.2.15. AMMONIA

The amount of ammonia present in the estuarine water sample was determined by phenol hypochlorite method (Solorzano, 1969). 5 ml of sample was taken. To this 0.2 ml of sodium nitroprusside and phenolic alcohol solution were added and mixed well. Then 0.5 ml of oxidant was added (4 ml of hypochlorite solution and 1 ml of sodium citrate solution). After 10 minutes the optical density at 640 nm was recorded in a spectrophotometer. From the recorded value the amount of ammonia present in the water sample was calculated as follows:

$$\text{Ammonia (mg/l)} = \frac{\text{Conc. of standard} \times \text{OD of unknown sample}}{\text{OD of known sample (standard)}}$$

3.2.16. SULPHATE

Sulphate present in the water sample was determined by turbidimetric method (APHA, 1985). 10 ml of water sample was taken and was diluted to 100 ml. 20 ml of this diluted sample 5 ml of conditioning reagent was added and mixed well. Put it on stirring apparatus. Add barium chloride crystals while stirring and continue the stirring for 1 minute. Measure the turbidity developed on colorimeter at 420 nm after stirring for 5 minutes.

$$\text{SO}_4^{2-} \text{ (mg/l)} = \frac{\text{SO}_4^{2-} \text{ mg} \times 1000}{\text{Volume of sample}} \times \text{Dilution factor}$$

3.2.17. MANGANSE, ZINC, COPPER AND IRON

Heavy metals present in the water samples were extracted following the methodology of Jan and Young (1978). 1 litre of water sample was filtered through a 0.45 millipore filter. Metals were extracted with 50 ml of 1% ammonium pyrrolidine dithiocarbamate ($\text{C}_5\text{H}_8\text{NS}_2\text{NH}_4$) by vigorously shaking for 15 minutes. The organic medium containing the extracted metal was separated. The metals were then brought to the aqueous medium by shaking with 1ml of 50% analar nitric acid. The aqueous layer was separated. It was made up to 15ml with distilled water. Then the heavy metals such as manganese, zinc, copper and iron were analyzed by aspirating into the Atomic Absorption Spectrophotometer (GBC932+). Standard metal solutions were used for calibration.

3.2.18 STATISTICAL ANALYSIS

The data obtained in the present study were subjected to relevant statistical analysis following the procedure given in Zar (1999). The statistical analyses followed were:

- Mean
- Standard Deviation
- Two way analysis of variance
- Correlation coefficient and
- Regression.

3.3. RESULT

Monthly atmospheric and water temperature were recorded in the sampling stations during the study period of two years from January 2010 to December 2011.

3.3.1. ATMOSPHERIC TEMPERATURE

The monthly fluctuation and average atmospheric temperature ($^{\circ}\text{C}$) recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig. 3.1 and 3.2. The atmospheric temperature recorded during 2010 ranged from 25.0°C in October and November to 29.0°C in March and April, 25.0°C in October and November to 29.0°C in April, from 25.0°C in August to 29.0°C in March and April at stations, S-I, S-II and S-III respectively. The monthly average atmospheric temperature recorded was high with $26.75\pm 1.38^{\circ}\text{C}$ at S-I and low with $26.66\pm 1.41^{\circ}\text{C}$ in S- II. In 2011, atmospheric temperature in S-I varied from a minimum of 25.0°C in July and October to a maximum of 29.0°C in February. In S-II, the atmospheric temperature ranged from a minimum of 24.5°C in November to a maximum of 29.0°C in February and March. In S-III, it varied from 24.5°C in November to a maximum of 29.50°C in February. The monthly average atmospheric temperature recorded was high with $26.875\pm 1.59^{\circ}\text{C}$ at S-III and low with $26.75\pm 1.40^{\circ}\text{C}$ and $26.75\pm 1.53^{\circ}\text{C}$ in S-I and S-II respectively.

Seasonal fluctuations in atmospheric temperature in sampling stations are provided in the Table 3.3. In 2010, during non monsoon period a minimum atmospheric temperature of $28.25\pm 0.95^{\circ}\text{C}$ was observed in S-I and the

maximum of 28.375 ± 0.62 °C and 28.375 ± 0.94 °C were noticed in S-II and S-III respectively. During southwest monsoon period a minimum of 25.625 ± 0.47 °C in S-III and a maximum of 26.50 ± 0.70 °C were noticed in S-I. The northeast monsoon period had a maximum atmospheric temperature of 26.125 ± 0.94 °C in S-III and a minimum of 25.5 ± 0.70 °C in S-I and S-II. In 2011, non monsoon period recorded minimum atmospheric temperature of 28.375 ± 0.62 °C in S-I and maximum atmospheric temperature of 28.5 ± 0.70 °C and 28.5 ± 1.08 °C in S-II and S-III respectively. The southwest monsoon period had a minimum of 26.0 ± 0.91 °C in S-I and a maximum of 26.25 ± 0.86 °C in S-II. The northeast monsoon period had a minimum of 25.5 ± 0.91 °C in S-II and a maximum of 26.0 ± 1.2 °C in S-III.

Two-way analysis of variance for the data on atmospheric temperature between the sampling stations showed no significant variation in both the years of study period ($F = 0.032$ and 0.429 ; $P > 0.05$). But the variation between seasons was statistically more significant ($F = 37.45$; $P < 0.01$ and $F = 173.71$; $P < 0.001$) in 2010 and 2011 (Table 3.3.a).

In the year 2010, atmospheric temperature showed a significant positive correlation ($P < 0.05$) with water temperature and carbon dioxide at all stations. It also showed significant positive correlation with sulphate at S-I and S-II and with salinity and electrical conductivity at S-II. It showed a significant negative correlation ($P < 0.05$) with dissolved oxygen at S-I and S-II, with nitrate at S-II and S-III, bicarbonate and copper at S-II and magnesium and zinc at S-III. In 2011, atmospheric temperature showed a significant positive correlation ($P <$

0.05) with water temperature, salinity and carbon dioxide at all stations, with sulphate at S-I and S-II, with electrical conductivity at S-I and with biological oxygen demand and iron at S-II. The correlation was significantly negative ($P < 0.05$) with dissolved oxygen at all stations, with ammonia and copper at S-I and S-II, with bicarbonate at S-II and S-III, with nitrite at S-I and with nitrate at S-III. With other parameters the correlation was not significant (Tables 3.24 to 3.29).

3.3.1. B) WATER TEMPERATURE

The monthly fluctuation and average water temperature recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig. 3.3 and 3.4. The water temperature recorded during 2010 ranged from 24.5 °C in November to 29.0 °C in April, from 24.5 °C in July to 28.5 °C in April and from 24.5 °C in July and August to 28.5 °C in April at station I, II and III respectively. The monthly average water temperature recorded was high with 26.25 ± 1.27 °C at S-I and low with 26.08 ± 1.29 °C in S- II. In 2011, water temperature in S-I varied from a minimum of 24.5 °C during July to a maximum of 28.5 °C during February. In S-II and S-III, the water temperature ranged from a minimum of 24.5 °C in November to a maximum of 29.50 °C in February. The monthly average water temperature recorded was high with 26.625 ± 1.49 °C at S-III and low with 26.33 ± 1.32 °C in S- I.

Table 3.4 provides seasonal fluctuations in water temperature in sampling stations during the study period. In 2010, during non monsoon period minimum water temperature of 27.5 ± 1.29 °C and 27.5 ± 1.08 °C were recorded in S-I and S-

III respectively and a maximum of 27.625 ± 0.85 °C in S-III. The southwest monsoon period had a minimum of 25.125 ± 0.75 °C in S-III and a maximum of 25.75 ± 0.5 °C in S- I. The northeast monsoon period had a minimum of 25.375 ± 0.75 °C in S-II and a maximum of 25.875 ± 0.75 °C in S-III. During 2011, non monsoon period recorded minimum water temperature of 27.875 ± 0.63 °C in S-I and a maximum of 28.25 ± 0.86 °C in S-II and S-III. In the same year the southwest monsoon period had a minimum of 25.5 ± 0.91 °C in S-I and a maximum (26.0 ± 0.91 °C) in S- II and S-III. The northeast monsoon period had a minimum of 25.25 ± 0.65 °C in S-II and a maximum of 26.675 ± 1.1 °C in S-III.

Data on two-way analysis of variance (Table.3.4.a) revealed that the variation in water temperature between stations was statistically not significant in both the years of study period ($F = 0.30$ and 1.138 ; $P > 0.05$). On the other hand, the variation between seasons was statistically more significant in 2010 and 2011 ($F = 56.11$; $P < 0.01$ and $F = 108.58$; $P < 0.001$).

During the year 2010, water temperature was significantly correlated ($P < 0.05$) positively with atmospheric temperature at all stations, with carbon dioxide, electrical conductivity and sulphate at S-I and S-II, calcium and bicarbonate at S-I and with salinity at S-II. But it showed a significant negative correlation ($P < 0.05$) with dissolved oxygen at S-I, nitrite at S-I and S-II, nitrate at S-II and S-III, copper at S-II and with magnesium and zinc at S-III. In 2011, water temperature showed a significant positive correlation ($P < 0.05$) with atmospheric temperature, salinity and carbon dioxide at all stations. It also significantly correlated ($P < 0.05$) positively with biological oxygen demand, phosphate,

sulphate and iron at S-II. The correlation was significantly negative ($P < 0.05$) with dissolved oxygen at all stations, with nitrite, ammonia and copper at S-I and S-II, nitrate at S-II and S-III and with bicarbonate at S-III (Tables.3.24 to 3.29).

3.3.2 pH

The monthly fluctuation and average water pH recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig. 3.5 and 3.6. During 2010, the pH fluctuated from 6.28 in April to 7.55 in March, from 6.22 in January to 7.4 in December, from 5.74 in January to 7.5 in December at S- I, S-II and S-III respectively. The monthly average pH recorded was high with 6.96 ± 0.49 at S-III and low with 6.93 ± 0.35 at S-II. In 2011, the pH at S-I varied from a minimum of 6.5 in June to a maximum of 7.42 in March. In S-II, the pH ranged from a minimum of 6.26 in January to a maximum of 7.47 in December. In S-III, it varied from 5.88 in January to 7.46 in December. The monthly average pH recorded was high with 6.91 ± 0.45 at S-III and low with 6.85 ± 0.30 at S –II.

Seasonal fluctuations of pH in sampling stations during the study period are shown in Table 3.5. During 2010 the non monsoon period showed minimum pH of 6.84 ± 0.76 in S-III and a maximum of 6.93 ± 0.63 in S-I. The southwest monsoon period showed minimum mean pH of 6.72 ± 0.20 in S-I and maximum (6.97 ± 0.21) in S-III. In northeast monsoon season, the mean pH value varied from 7.07 ± 0.46 in S-III to 7.19 ± 0.26 in S-I. In 2011, during non monsoon period minimum pH value of 6.51 ± 0.49 was recorded in S-III and a maximum of 6.96 ± 0.37 in S-I. The southwest monsoon period had a minimum of 6.66 ± 0.20

in S-I and a maximum of 7.0 ± 0.29 in S-III. The northeast monsoon period had a minimum of 7.03 ± 0.20 in S-I and a maximum of 7.21 ± 0.26 in S-III.

Table 3.5.a provides data on two way analysis for the pH recorded in the sampling stations as a function of seasons. The results revealed that the variations in pH between stations and seasons were not statistically significant in both the years of study period ($F = 0.062$ and 0.067 ; $F = 0.592$ and 2.859 ; $P > 0.05$).

During 2011 pH showed a significant positive correlation ($P < 0.05$) with dissolved oxygen at S-II and S-III. But it showed a significant negative correlation with silicate at S-I and sulphate at S-II (Tables.3.24 to 3.29).

3.3.3 SALINITY

The monthly fluctuation and average salinity recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig. 3.7 and 3.8. The salinity recorded during 2010 ranged from 1.8 ppt in June to 7.8 ppt in December, from 1.2 ppt in October to 7.4 ppt in December, from 1.3 ppt in November to 4.3 ppt in April at stations I, II and III respectively. The monthly average salinity recorded was high with 4.825 ± 1.99 ppt at S-I and low with 3.62 ± 0.84 ppt in S-III. In 2011, at S-I the salinity varied from a minimum of 1.77ppt during June to a maximum of 7.43 ppt during April. In S-II, the salinity ranged from a minimum of 1.67 ppt in October to a maximum of 6.73 ppt in April. In S-III, it varied from 1.83 ppt in November to 4.44 ppt in April. The monthly average salinity recorded was high with 4.81 ± 1.84 ppt at S-I and low with 3.39 ± 0.98 ppt in S-III.

Seasonal fluctuations in salinity content in sampling stations are shown in Table 3.6. In 2010, higher salinity was recorded during non-monsoon season, the mean salinity content varied from 3.98 ± 0.40 ppt in S-III to 6.03 ± 1.10 ppt in S-I. The southwest monsoon period showed minimum mean salinity content of 3.33 ± 0.96 ppt in S-II and maximum (4.03 ± 0.17 ppt) in S-III. Northeast monsoon period showed minimum mean salinity of 2.87 ± 1.13 ppt in S-III and a maximum of 4.5 ± 2.2 ppt in S-I. In 2011, during non monsoon period minimum salinity of 4.20 ± 0.25 ppt was recorded in S-III and a maximum of 6.23 ± 0.88 ppt in S-I. During southwest monsoon period a minimum of 3.05 ± 1.21 ppt and a maximum of 4.15 ± 2.43 ppt were recorded in S-III and S-I respectively. The northeast monsoon period had a minimum of 2.84 ± 1.65 ppt in S-II and a maximum of 4.07 ± 1.37 ppt in S-I.

The two-way analysis of variance revealed that the variation in salinity content of water samples between stations was statistically not significant in 2010 ($F = 2.192$; $P > 0.05$), whereas; it was significant in 2011 ($F = 7.695$; $P < 0.05$). Likewise in 2010 the variations between seasons was statistically not significant ($F = 5.140$; $P > 0.05$) and it was more significant in 2011 ($F = 19.017$; $P < 0.01$) (Table 3.6.a).

In the year 2010, salinity showed a significant positive correlation ($P < 0.05$) with electrical conductivity at all stations. It also showed significant positive correlation with carbon dioxide at S-I and S-II, with calcium, sulphate, manganese and zinc at S-I and with atmospheric and water temperature, magnesium and iron at S-II. But it showed a significant negative correlation

($P < 0.05$) with dissolved oxygen at S-III, with copper at S-I and S-II, with silicate and ammonia at S-I and with nitrite, sulphate and zinc at S-III. During the year 2011, salinity showed significant positive correlation ($P < 0.05$) with atmospheric and water temperature. It also showed significant positive correlation ($P < 0.05$) with electrical conductivity, calcium, and magnesium at S-I and S-II, with sulphate, manganese and zinc at S-I, with carbon dioxide at S-II and S-III and with iron at S-II. The correlation was significantly negative ($P < 0.05$) with ammonia and copper at S-I and S-II, with dissolved oxygen, silicate and nitrite at S-I (Tables.3.24 to 3.29).

3.3.4 DISSOLVED OXYGEN

The monthly fluctuation and average dissolved oxygen content recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.9 and 3.10. During 2010, the dissolved oxygen content in S- I varied from a minimum of 2.55 ml/l in February to a maximum of 6.53 ml/l in November. In S - II, the oxygen content ranged from a minimum of 2.81ml/l to a maximum of 7.03 ml/l in June and November respectively. In S - III, it varied from 1.68 ml/l in June to 7.31 ml/l in November. The maximum monthly average dissolved oxygen content registered was 4.596 ± 1.30 ml/l at S-II against a minimum of 3.752 ± 1.7 ml/l at S-III. During 2011, at S-I the dissolved oxygen content varied from a minimum of 3.11ml/l in February to a maximum of 6.133 ml/l in December. In S-II, the oxygen content ranged from a minimum of 2.83 ml/l in June to a maximum of 6.81 ml/l in October. In S-III, it varied from 2.15 ml/l in

January to 6.64 ml/l in November. The monthly average dissolved oxygen content ranged from 4.917 ± 1.4 ml/l in S-II to 4.137 ± 1.57 ml/l in S-III.

Seasonal fluctuations in oxygen content in sampling stations during the study period are shown in Table 3.7. During the first year, the non monsoon period registered a minimum oxygen content of 2.46 ± 0.54 ml/l in S-III and a maximum of 3.86 ± 0.36 ml/l in S-II. The southwest monsoon period showed minimum oxygen content of 3.37 ± 1.66 ml/l in S-III and a maximum of 4.08 ± 0.75 ml/l in S-I. In the northeast monsoon season, it varied from 5.43 ± 1.32 ml/l in S-III to 6.06 ± 0.39 ml/l in S-I. During the second year, the non monsoon period registered a minimum oxygen content of 2.76 ± 0.61 ml/l in S-III and a maximum of 3.86 ± 0.36 ml/l in S-II. The southwest monsoon period showed a minimum of 3.617 ± 0.68 ml/l in S-III and a maximum of 4.45 ± 1.40 ml/l in S-II. The northeast monsoon period had a minimum of 6.037 ± 0.72 ml/l in S-III and a maximum of 6.45 ± 0.55 ml/l in S-II.

The two-way ANOVA test revealed that dissolved oxygen content of water samples as a function of variation between stations was statistically significant in 2010 and 2011 ($F = 10.599$ and 9.22 ; $P < 0.05$). Likewise the variation between seasons was also statistically significant in both the years of study period ($F = 87.572$ and 118.36 ; $P < 0.001$) (Table 3.7.a).

In 2010, dissolved oxygen showed a significant positive correlation ($P < 0.05$) with bicarbonate at S-II and with nitrite, sulphate at S-III. It showed a negative correlation ($P < 0.05$) with atmospheric temperature and carbon dioxide at S-I and S-II, water temperature at S-I, sulphate at S-II and with salinity and

ammonia at S-III. In 2011, dissolved oxygen showed a significant positive correlation ($P < 0.05$) with pH at S-II and S-III, bicarbonate at S-II and with sulphate at S-III. The correlation was significantly negative ($P < 0.05$) with atmospheric and water temperature at all stations, with carbon dioxide and sulphate at S-I and S-II, with salinity at S-I and with electrical conductivity at S-III (Tables.3.24 to 3.29).

3.3.5 CARBON DIOXIDE

The monthly fluctuation and average carbon dioxide content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig3.11 and 3.12. The carbon dioxide estimated during 2010 ranged from 1.0 ppm in June, October and November to 3.0 ppm in February, from 1.0 ppm in July, October and November to 3.5 ppm in March, from 1.5 ppm in October and November to 4.0 ppm in February at stations I, II and III respectively. The monthly average CO₂ content was maximum (2.75 ± 0.81 ppm) in S-III and a minimum of 1.616 ± 0.64 ppm in S-I. In 2011, carbon dioxide content in S-I varied from a minimum of 1.0 ppm during August and November to a maximum of 2.5 ppm during February. In S-II, the carbon dioxide content ranged from a minimum of 1.00 ppm in July, October and November to a maximum of 3.5 ppm in February. In S-III, it varied from 1.5 ppm in November to 3.5 ppm in March. The monthly average CO₂ content was maximum (2.48 ± 0.61 ppm) in S-III and a minimum of 1.60 ± 0.48 ppm in S-I.

Seasonal fluctuations in carbon dioxide in sampling stations are provided in Table 3.8. In 2010, during non-monsoon period minimum carbon dioxide of

2.25±0.64 ppm was recorded in S-I and a maximum of 3.38±0.47 ppm in S-III. The southwest monsoon period had a minimum of 1.43±0.43 ppm in S-I and a maximum of 2.63±0.95 ppm in S-III. The northeast monsoon period had a minimum of 1.18±0.23ppm in S-I and a maximum of 2.25±0.86 ppm in S-III. In 2011, during non-monsoon period minimum carbon dioxide of 2.0±0.40 ppm was registered in S-I and a maximum of 3.02±0.36 ppm in S-III. During southwest monsoon period a minimum of 1.55±0.52 ppm in S-I and a maximum (2.25±0.61 ppm) in S-III were recorded. The northeast monsoon period had a minimum of 1.25±0.20 ppm in S-I and a maximum of 2.15±0.50 ppm in S-III.

The two-way analysis of variance for the data on carbon dioxide content in water samples as a function of variation between stations was statistically significant in both the years of study ($F = 18.59$; $P < 0.01$ and $F = 13.994$; $P < 0.05$). Likewise the variation between seasons was also statistically significant in both the periods of study ($F = 23.75$ and 20.149 ; $P < 0.01$) (Table 3.8.a).

The carbon dioxide showed a significant positive correlation ($P < 0.05$) with atmospheric temperature at all stations, with water temperature, salinity at S-I and S-II, electrical conductivity and calcium at S-I, sulphate and Iron at S-II. On the other hand it showed a significant negative correlation ($P < 0.05$) with nitrite at all stations, dissolved oxygen and copper at S-I and S-II, nitrate at S-II and calcium at S-III during 2010. In 2011, the correlation was significantly positive ($P < 0.05$) with atmospheric and water temperature at all stations, with salinity at S-II and S-III and with biological oxygen demand and sulphate at S-II. It showed a significant negative correlation ($P < 0.05$) with dissolved oxygen and

copper at S-I and S-II and with bicarbonate, nitrate and ammonia at S-II (Tables.3.24 to 3.29).

3.3.6 BIOLOGICAL OXYGEN DEMAND (BOD)

The monthly fluctuation and average BOD observed in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.13 and 3.14. During 2010, the BOD varied from a minimum of 0.28 ml/l in April, May and September to a maximum of 0.99 ml/l in August in S-I. In S-II, the BOD ranged from a minimum of 0.28 ml/l in June to a maximum of 2.26 ml/l in March. In S-III, BOD varied from 0.56 ml/l in April to 1.98 ml/l in March. The monthly average BOD was maximum in S-III with 1.18 ± 0.47 ml/l and a minimum of 0.50 ± 0.23 ml/l in S-I. During 2011, the BOD in S-I varied from a minimum of 0.37 ml/l in May to a maximum of 0.82 ml/l in June. In S-II, the BOD ranged from a minimum of 0.28 ml/l in June to a maximum of 2.62 ml/l in March. In S-III, it varied from 0.76 ml/l in May to 2.03 ml/l in March. The monthly average BOD was maximum in S-III with 1.19 ± 0.36 ml/l and a minimum of 0.53 ± 0.14 ml/l in S-I.

Seasonal fluctuations in biological oxygen demand in the sampling stations are shown in Table 3.9. During 2010, the non monsoon period showed a minimum mean biological oxygen demand of 0.49 ± 0.14 ml/l in S-I against the maximum of 1.37 ± 0.66 ml/l in S- II. The southwest monsoon period showed a minimum mean value of 0.667 ± 0.031 ml/l in S-I and a maximum of 1.12 ± 0.22 ml/l in S-III. In the northeast monsoon season, it varied from 0.35 ± 0.06 ml/l at S-I to 1.35 ± 0.54 ml/l at S-III. In 2011, during the non monsoon period, minimum

biological oxygen demand of 0.53 ± 0.05 ml/l was recorded in S- I and a maximum of 1.45 ± 0.82 ml/l in S- II. The southwest monsoon period had a minimum of 0.63 ± 0.21 ml/l in S- I and a maximum of 1.16 ± 0.28 ml/l in S-III. The northeast monsoon period had a minimum of 0.427 ± 0.02 ml/l in S-I and a maximum of 1.26 ± 0.21 ml/l in S-III.

The two-way analysis of variance for the data on biological oxygen demand of water samples as a function of variation between stations and seasons were statistically not significant ($F = 4.694$ and 5.737 ; $F = 0.239$ and 0.678 ; $P > 0.05$) during 2010 and 2011 (Table 3.9.a).

Biological oxygen demand had a significant positive correlation ($P < 0.05$) with silicate at S-I and with calcium at S-III during 2010. In the year, 2011 a significant positive correlation ($P < 0.05$) was observed with silicate and sulphate at S-I and with atmospheric temperature, water temperature and carbon dioxide at S-II (Tables.3.24 to 3.29).

3.3.7 BICARBONATE

The monthly fluctuation and average bicarbonate content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.15 and 3.16. The bicarbonate estimated during 2010 ranged from 36.61 ppm in November to 115.9 ppm in April, from 24.0 ppm in February to 183.05 ppm in October, from 30.0 ppm in February to 244.0 ppm in October at S- I, S-II and S- III respectively. The monthly average bicarbonate recorded was high with 127.6 ± 61.11 ppm at S-III and low with 59.12 ± 20.25 ppm in S-I. In 2011, bicarbonate content in S-I varied from a minimum of 44.78 ppm during March to a maximum

of 150.52 ppm during April. In S-II, the bicarbonate content ranged from a minimum of 33.40 ppm in February to a maximum of 151.62 ppm in October. In S-III, it varied from 36.98 ppm in February to 238.53 ppm in October. The monthly average bicarbonate recorded was high with 127.73 ± 59.0 ppm at S-III and low with 62.24 ± 28.33 ppm in S-I.

Table 3.10 provides seasonal fluctuations in bicarbonate content in sampling stations during the study period. Non-monsoon period showed minimum mean bicarbonate content of 45.66 ± 18.46 ppm in S- II and a maximum of 115.81 ± 65.75 ppm in S-III. The southwest monsoon period showed minimum mean bicarbonate content of 54.92 ± 4.98 ppm in S-I and a maximum of 126.61 ± 56.22 ppm in S-III. In northeast monsoon season, the mean bicarbonate content varied from 57.97 ± 14.53 ppm in S- I to 140.33 ± 76.21 ppm in S-III. In 2011, during non-monsoon period minimum bicarbonate content of 48.27 ± 15.90 ppm was estimated in S-II and a maximum of 116.30 ± 61.23 ppm in S-III. The southwest monsoon period had a minimum of 52.61 ± 8.802 ppm in S-II and a maximum of 126.33 ± 57.72 ppm in S-III. The northeast monsoon period had a minimum of 58.16 ± 6.75 ppm in S-I and a maximum of 140.57 ± 72.79 ppm in S-III.

The two-way ANOVA revealed that HCO_3 content of water samples as a function of variation between stations was statistically significant in both the years of study period ($F = 16.258$ and 14.55 ; $P < 0.05$). But the variation between seasons was not statistically significant in 2010 and 2011 ($F = 1.988$ and 1.29 ; $P > 0.05$) (Table 3.10.a).

Bicarbonate showed a significant positive correlation ($P < 0.05$) with water temperature, electrical conductivity and magnesium at S-I, dissolved oxygen at S-II and with calcium at S-I and S-III. It showed a significant negative correlation ($P < 0.05$) with sulphate at S-II. During 2011, bicarbonate was positively correlated ($P < 0.05$) significantly with electrical conductivity and magnesium at S-I, dissolved oxygen at S-II and with calcium at S-I and S-III. But it exhibited a significant negative correlation ($P < 0.05$) with atmospheric temperature at S-II and S-III, with carbon dioxide and sulphate at S-II and with water temperature at S-III (Tables 3.24 to 3.29).

3.3.8. ELECTRICAL CONDUCTIVITY (EC)

The monthly fluctuation and average electrical conductivity noticed in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.17 and 3.18. The electrical conductivity recorded during 2010 ranged from 0.265 ds/m in November to 10.42 ds/m in April, from 0.614 ds/m in November to 10.15 ds/m in April, from 1.507 ds/m in November to 5.02 ds/m in April at stations I, II and III respectively. The monthly average electrical conductivity recorded was high with 3.14 ± 2.93 ds/m at S-I and low with 2.9 ± 276 ds/m in S-II. During 2011, in S-I the electrical conductivity varied from a minimum of 0.44 ds/m in October to a maximum of 9.851 ds/m during April. In S-II, the electrical conductivity ranged from a minimum of 0.675 ds/m in October to a maximum of 10.413 ds/m in April. In S-III, it varied from 1.569 ds/m in September to 5.107

ds/m in April. The monthly average electrical conductivity recorded was high with 3.54 ± 2.79 ds/m at S-I and low with 3.09 ± 1.19 ds/m in S-III.

Seasonal fluctuations in electrical conductivity in sampling stations are provided in Table 3.11. In 2010, the non monsoon period showed minimum mean electrical conductivity of 3.47 ± 1.60 ds/m in S- III and a maximum of 5.14 ± 3.66 ds/m in S-I. The southwest monsoon period showed minimum mean electrical conductivity of 2.08 ± 1.33 ds/m in S-I and the maximum of 3.67 ± 1.17 ds/m in S-III. In north-east monsoon season, the mean electrical conductivity varied from 1.90 ± 0.42 ds/m in S- III to 2.20 ± 2.89 ds/m in S-I. In 2011, during non monsoon period minimum electrical conductivity of 3.68 ± 1.31 ds/m was recorded in S-III against the maximum of 5.34 ± 3.09 ds/m in S-I. During southwest monsoon period a minimum of 2.26 ± 0.86 ds/m in S-II and a maximum of 3.68 ± 0.72 ds/m in S- III were noticed. The northeast monsoon period had a minimum of 1.88 ± 0.26 ds/m in S-III and a maximum of 2.65 ± 2.54 in S-II.

The two-way analysis of variance for the data on electrical conductivity of water samples as a function of variation between stations and seasons were statistically not significant ($F = 0.0528$ and 0.268 ; $F = 5.473$ and 6.501 ; $P > 0.05$) during 2010 and 2011 (Table 3.11.a).

Electrical conductivity exhibited a significant positive correlation ($P < 0.05$) with salinity at all stations, with water temperature and magnesium at S-I and S-II, with carbon dioxide, bicarbonate, calcium and sulphate at S-I, with atmospheric temperature at S-II and with silicate at S-III. It showed a significant negative correlation ($P < 0.05$) with copper at S-I and with zinc at S-III in 2010.

In the year 2011, electrical conductivity was significantly correlated ($P < 0.05$) positively with salinity, magnesium and calcium at S-I and S-II, with atmospheric temperature, bicarbonate and zinc at S-I, iron at S-II and with silicate at S-III. It showed a significant negative correlation ($P < 0.05$) with copper at S-I and S-II, with silicate, nitrite and ammonia at S-I and with dissolved oxygen and zinc at S-III (Tables 3.24 to 3.29).

3.3.9 CALCIUM

The monthly fluctuation and average calcium content recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.19 and 3.20. The calcium estimated during 2010 ranged from 12.02 ppm in July to 66.12 ppm in April, from 10.2 ppm in October to 140.27 ppm in May, from 20.03 ppm in September to 160.3 ppm in October at S- I, S-II and S-III respectively. The monthly average calcium recorded was high with 64.14 ± 37.35 ppm at S-III and low with 30.88 ± 16.13 ppm at S-I. In 2011, at S-I the calcium content varied from a minimum of 12.37 ppm during July to a maximum of 64.27 ppm during April. In S-II, the calcium content ranged from a minimum of 9.79 ppm in October to a maximum of 69.12 ppm in December. In S-III, it varied from 20.77 ppm in September and 167.02 ppm in October. The monthly average calcium recorded was high with 66.60 ± 37.7 ppm at S-III and low with 30.84 ± 15.38 ppm at S-I.

Seasonal fluctuations in calcium content in sampling stations during the study period are shown in Table 3.12. In 2010, during non-monsoon period the minimum calcium content of 41.57 ± 16.71 ppm was recorded in S-I against the

maximum of 50.10 ± 6.94 ppm in S-III. The southwest monsoon period had a minimum of 23.04 ± 10.66 ppm in S-I and a maximum of 67.63 ± 50.6 ppm in S-II. The northeast monsoon period had a minimum of 28.05 ± 17.7 ppm in S-I and a maximum of 82.15 ± 58.21 ppm in S-III. In 2011, during non monsoon period the minimum calcium content of 40.18 ± 16.16 ppm was registered in S-I and a maximum of 55.24 ± 1.35 ppm was noticed in S-III. During the same year the southwest monsoon period had a minimum of 23.16 ± 10.54 ppm in S-I and a maximum of 60.98 ± 29.98 ppm in S-III. The northeast monsoon period had a minimum of 29.18 ± 17.20 ppm in S-I and a maximum of 83.57 ± 60.95 ppm in S-III.

The two-way analysis of variance for the data on calcium content of water samples as a function of variation between stations and seasons were not statistically significant in both the years of study period ($F = 2.309$ and 5.40 ; $F = 0.063$ and 0.095 ; $P > 0.05$) (Table 3.12.a).

In the year 2010, calcium showed a significant positive correlation ($P < 0.05$) with biological oxygen demand and bicarbonate at S-I and S-III, with magnesium at S-I and S-II, with water temperature, salinity, carbon dioxide, sulphate, manganese and electrical conductivity at S-I and with nitrite at S-III. But it showed a significant negative correlation ($P < 0.05$) with silicate and copper in S-I, phosphate at S-II and with carbon dioxide in S-III. In 2011, calcium was significantly correlated ($P < 0.05$) positively with salinity, electrical conductivity and magnesium at S-I and S-II, bicarbonate at S-I and S-III and with manganese and zinc at S-I. On the other hand it showed a significant negative

correlation ($P < 0.05$) with copper at S-I and S-II and silicate nitrite and ammonia at S-I (Tables.3.24 to 3.29).

3.3.10 MAGNESIUM

The monthly fluctuation and average magnesium content observed in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.21 and 3.22. The magnesium estimated during 2010 ranged from 49.83 ppm in September to 270.40 ppm in May, from 20.66 ppm in February to 225.2 ppm in April, from 24.3 ppm in October to 98.42 ppm in June at stations I, II and III respectively. The monthly average magnesium recorded was high (121 ± 79.59 ppm) at S-I and low (52.60 ± 24.61 ppm) in S- III. In 2011, magnesium content in S-I varied from a minimum of 52.88 ppm during September to a maximum of 269.23 ppm during April. In S-II, the magnesium content ranged from a minimum of 27.85 ppm in February to a maximum of 220.49 ppm in April. In S- III, it varied from 25.87 ppm in October to 98.46 ppm in June. The monthly average magnesium recorded was high with 123 ± 78.44 ppm at S-I and low with 53.44 ± 22.94 ppm in S- III.

Table 3.13 provides seasonal fluctuations in magnesium content in sampling stations during the study period. In 2010, during non monsoon period the minimum magnesium content of 33.92 ± 7.80 ppm was registered in S-III and a maximum of 134.99 ± 87.93 ppm in S-I. During southwest monsoon period had a minimum of 82.27 ± 10.86 ppm in S-III and a maximum of 139.64 ± 91.50 ppm in S-I were noticed. The northeast monsoon period had a minimum of 41.62 ± 15.58 ppm in S-III and a maximum of 88.61 ± 70.58 ppm in S-I. In 2011, during non

monsoon period the minimum magnesium content of 37.81 ± 6.85 ppm was noticed in S-III against the maximum of 140.36 ± 86.06 ppm in S-I. The southwest monsoon period had a minimum of 81.12 ± 11.89 ppm in S-III and a maximum 141.28 ± 88.85 ppm in S- I. Likewise the northeast monsoon period had a minimum of 41.38 ± 14.14 ppm in S-III and a maximum of 90.09 ± 70.53 ppm in S-I.

Two-way analysis of variance for the data on magnesium content of water samples as a function of variation between stations was statistically significant in both the years ($F = 9.983$ and 11.486 ; $P < 0.05$). On the other hand the variation between seasons was statistically not significant in both the years of study period ($F = 2.185$ and 2.465 $P > 0.05$) (Table 3.13.a).

Magnesium showed a significant positive correlation ($P < 0.05$) with electrical conductivity and calcium at S-I and S-II, with bicarbonate at S-I, with salinity at S-II and with silicate at S-III. On the other hand it showed a significant negative correlation ($P < 0.05$) with atmospheric temperature, water temperature and iron at S-III during 2010. In 2011, the correlation was significantly positive ($P < 0.05$) with salinity, electrical conductivity and calcium at S-I and S-II, with bicarbonate at S-I and with silicate at S-III. It showed a significant negative correlation ($P < 0.05$) with nitrite at S-I and S-III and with ammonia at S-I (Tables.3.24 to 3.29).

3.3.11 SILICATE

The monthly fluctuation and average silicate content recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2;

Fig.3.23 and 3.24. The silicate estimated during 2010 ranged from a minimum (29.24 $\mu\text{g/l}$) in December to 85.10 $\mu\text{g/l}$ in June, from 20.8 $\mu\text{g/l}$ in January to 87.94 $\mu\text{g/l}$ in July, from 19.60 $\mu\text{g/l}$ in February to 71.48 $\mu\text{g/l}$ in July at S- I, S-II and S-III respectively. The monthly average silicate content was maximum 47.67 \pm 16.11 $\mu\text{g/l}$ in S-I and a minimum of 41.49 \pm 19.69 $\mu\text{g/l}$ in S-III. In 2011, silicate content in S-I varied from a minimum (29.16 $\mu\text{g/l}$) in December to a maximum of 86.0 $\mu\text{g/l}$ in June. In S-II, the silicate content ranged from a minimum (22.53 $\mu\text{g/l}$) in February to a maximum of 88.07 $\mu\text{g/l}$ in July. In S-III, it varied from 22.40 $\mu\text{g/l}$ in February to a minimum of (71.77 $\mu\text{g/l}$) in July. The monthly average silicate content was maximum 45.61 \pm 20.63 $\mu\text{g/l}$ in S-II against the minimum of 41.33 \pm 18.88 in $\mu\text{g/l}$ in S-III.

Table 3.14 shows the seasonal fluctuations in silicate content in sampling stations. In 2010, during non monsoon period the minimum silicate content of 31.26 \pm 20.02 $\mu\text{g/l}$ was estimated in S-III against the maximum of 37.85 \pm 4.35 $\mu\text{g/l}$ in S-I. During southwest monsoon period a minimum of 60.27 \pm 13.56 $\mu\text{g/l}$ in S-III and a maximum of 63.79 \pm 17.56 $\mu\text{g/l}$ in S- I were recorded. The northeast monsoon period had a minimum of 32.97 \pm 11.45 $\mu\text{g/l}$ in S-III and a maximum of 41.38 \pm 9.11 $\mu\text{g/l}$ in S-I. In 2011, during non monsoon period the minimum silicate content of 33.88 \pm 21.76 $\mu\text{g/l}$ was registered in S-III and a maximum of 38.38 \pm 3.94 $\mu\text{g/l}$ was noticed in S-I. The southwest monsoon period had a minimum of 57.69 \pm 13.41 $\mu\text{g/l}$ in S-III and a maximum 64.24 \pm 23.14 $\mu\text{g/l}$ in S- II; whereas, the northeast monsoon period had a minimum of 32.45 \pm 10.89 $\mu\text{g/l}$ in S-III and a maximum of 41.75 \pm 9.50 $\mu\text{g/l}$ in S-I.

The two-way analysis of variance for the data on silicate content in water samples as a function of variation between stations was statistically significant in both the years of study period ($F = 15.993$ and 9.549 ; $P < 0.05$). But the variation between seasons was statistically more significant in both the study periods ($F = 397.961$ and 183.81 ; $P < 0.001$) (Table 3.14.a).

Silicate exhibited a significant positive correlation ($P < 0.05$) with copper at all stations, with ammonia at S-I and S-II, with biological oxygen demand at S-I and with electrical conductivity and magnesium at S-III. It also showed a significant negative correlation ($P < 0.05$) with manganese, zinc and iron at all stations and with salinity and calcium at S-I during 2010. In 2011, the correlation was significantly positive ($P < 0.05$) with copper at all stations, with nitrite at S-I and S-II, with biological oxygen demand and ammonia at S-I and with electrical conductivity and magnesium at S-III. It also showed a significant negative correlation ($P < 0.05$) with manganese, zinc and iron at all stations, with pH, salinity, electrical conductivity and calcium at S-I and with nitrite at S-III (Tables.3.24 to 3.29).

3.3.12 PHOSPHATE

The monthly fluctuation and average phosphate content noticed in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.25 and 3.26. The phosphate estimated during 2010 ranged from ($0.302 \mu\text{g/l}$) in September to $3.28 \mu\text{g/l}$ in December, from $0.176 \mu\text{g/l}$ in August to $2.106 \mu\text{g/l}$ in June, from $0.168 \mu\text{g/l}$ in August to $2.106 \mu\text{g/l}$ in June at stations I, II and III

respectively. The monthly average phosphate content was maximum 1.50 ± 0.98 $\mu\text{g/l}$ in S-I and a minimum of $0.94 \pm 0.53 \mu\text{g/l}$ in S-II. In 2011, phosphate content in S-I ranged from a minimum ($0.55 \mu\text{g/l}$) in April to a maximum of $3.25 \mu\text{g/l}$ in December. In S-II, the phosphate content ranged from a minimum of 0.44 in July to a maximum ($2.20 \mu\text{g/l}$) in June. In S-III, it varied from ($0.28 \mu\text{g/l}$) in July to $2.25 \mu\text{g/l}$ in June. The monthly average phosphate content was maximum $1.84 \pm 0.83 \mu\text{g/l}$ in S-I against a minimum of $1.15 \pm 0.56 \mu\text{g/l}$ in S-III.

Seasonal fluctuations in phosphate content in sampling stations during the study period are shown in Table 3.15. In 2010, non monsoon period recorded minimum phosphate content of $1.08 \pm 0.16 \mu\text{g/l}$ in S-II; whereas, the maximum phosphate content of $1.32 \pm 0.70 \mu\text{g/l}$ was recorded in S-I. The southwest monsoon period had a minimum of $0.74 \pm 0.09 \mu\text{g/l}$ in S-III and a maximum of $1.26 \pm 0.92 \mu\text{g/l}$ in S-I. Similarly the northeast monsoon period had a minimum of $1.04 \pm 0.35 \mu\text{g/l}$ in S-III and a maximum of $2.05 \pm 1.28 \mu\text{g/l}$ in S-I. In 2011, during non monsoon period the minimum phosphate content of $1.39 \pm 0.17 \mu\text{g/l}$ was estimated in S-III and a maximum of $1.69 \pm 0.84 \mu\text{g/l}$ in S-I. During this year, the southwest monsoon period had a minimum of $0.92 \pm 0.89 \mu\text{g/l}$ in S-III and a maximum ($1.50 \pm 0.71 \mu\text{g/l}$) in S-I. The northeast monsoon period had a minimum of $1.06 \pm 0.35 \mu\text{g/l}$ in S-II and a maximum of $2.32 \pm 0.92 \mu\text{g/l}$ in S-I.

Two-way analysis of variance for the data on phosphate content in water samples as a function of variation between stations and seasons were statistically not significant in both the years of study period ($F = 4.55$ and 3.779 ; $F = 1.937$ and 1.373 ; $P > 0.05$) (Table 3.15.a).

Phosphate showed a significant positive correlation ($P < 0.05$) with nitrate, zinc and iron at S-I and it showed a significant negative correlation ($P < 0.05$) with calcium at S-II and nitrate at S-III during 2010. In 2011, it was significantly correlated ($P < 0.05$) positively with nitrate at S-I and with water temperature and sulphate at S-II. On the other hand it showed a significant negative correlation ($P < 0.05$) with nitrate at S-II and S-III and with nitrite and ammonia at S-II (Tables.3.24 to 3.29).

3.3.13 NITRITE

The monthly fluctuation and average nitrite content recorded in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.27 and 3.28. The nitrite estimated during 2010 ranged from (0.04 μ g/l) in February, March and April to (0.57 μ g/l) in August, from (0.026 μ g/l) in September to (0.858 μ g/l) in August and from 0.015 μ g/l in March to 0.14 μ g/l in November at stations I, II and III respectively. The monthly average nitrite content was maximum (0.23 \pm 0.02 μ g/l) in S-II and minimum (0.07 \pm 0.04 μ g/l) in S-III. During 2011, nitrite content in S-I varied from a minimum of 0.043 μ g/l in February to maximum (0.534 μ g/l) in July. In S-II, the nitrite content ranged from 0.037 μ g/l in December and 0.718 μ g/l in July. In S-III, it was maximum 0.025 μ g/l in August to minimum 0.23 μ g/l in February. The monthly average nitrite content was maximum 0.176 \pm 0.16 μ g/l in S-I against the minimum of 0.13 \pm 0.07 μ g/l in S-III.

Table 3.16 shows the seasonal fluctuations in nitrite content in sampling stations. In 2010, during non monsoon period the minimum nitrite content of 0.03 ± 0.01 $\mu\text{g/l}$ was estimated in S-III; whereas it was maximum (0.07 ± 0.005 $\mu\text{g/l}$) in S-II. During southwest monsoon period a minimum of 0.05 ± 0.02 $\mu\text{g/l}$ in S-III and a maximum of 0.42 ± 0.4 $\mu\text{g/l}$ in S- II were noticed. The northeast monsoon period had a minimum of 0.11 ± 0.04 $\mu\text{g/l}$ in S-III and a maximum of 0.206 ± 0.23 $\mu\text{g/l}$ in S-II. In 2011, during non monsoon period the minimum nitrite content of 0.049 ± 0.005 $\mu\text{g/l}$ was registered in S-I against the maximum of 0.189 ± 0.058 $\mu\text{g/l}$ in S-III. The southwest monsoon period had a minimum of 0.172 ± 0.057 $\mu\text{g/l}$ in S-III and a maximum (0.291 ± 0.31 $\mu\text{g/l}$) in S-II. The northeast monsoon period had a minimum of 0.144 ± 0.039 $\mu\text{g/l}$ in S-III and a maximum of 0.218 ± 0.121 $\mu\text{g/l}$ in S-I.

The two-way analysis of variance for the data on nitrite content in water samples as a function of variation between stations was statistically not significant in both the years of study period ($F = 2.538$ and 0.01 ; $P > 0.05$). Similarly the variation between seasons was also not statistically significant ($F = 4.178$ and 2.66 ; $P > 0.05$) during 2010 and 2011 (Table 3.16.a).

In 2010 nitrite had a significant positive correlation ($P < 0.05$) with copper at S-I and S-II, with nitrate at S-II, with dissolved oxygen, calcium and sulphate at S-III. It showed a significant negative correlation ($P < 0.05$) with carbon dioxide at all stations, with water temperature at S-I and S-II and with salinity at S-III. During 2011, it showed a significant positive correlation ($P < 0.05$) with silicate, ammonia and copper at S-I and S-II, with nitrate at S-II and

with manganese, zinc and iron at S-III. Nitrite showed a significant negative correlation ($P < 0.05$) with water temperature, zinc and iron at S-I and S-II, with magnesium at S-I and S-III, with atmospheric temperature, salinity electrical conductivity, calcium, and manganese at S-I, phosphate at S-II and with silicate and copper at S-III (Tables.3.24 to 3.29).

3.3.14 NITRATE

The monthly fluctuation and average nitrate content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.29 and 3.30. In 2010, the nitrate content ranged from 1.25 $\mu\text{g/l}$ in April to 5.78 $\mu\text{g/l}$ in November, from 0.21 $\mu\text{g/l}$ in May to 7.82 $\mu\text{g/l}$ in July and from 0.98 $\mu\text{g/l}$ in June to 5.23 $\mu\text{g/l}$ in July at stations I, II and III respectively. The monthly average nitrate content was maximum $3.05 \pm 1.8 \mu\text{g/l}$ in S-I and a minimum of $2.24 \pm 2.203 \mu\text{g/l}$ in S-II. During 2011, in S-I nitrate content varied from a minimum of 1.39 $\mu\text{g/l}$ in March to a maximum of 5.61 $\mu\text{g/l}$ in November. In S-II, the nitrate content ranged from a minimum of 0.56 $\mu\text{g/l}$ in April to a maximum of 7.61 $\mu\text{g/l}$ in July. In S-III, nitrate content recorded was minimum (0.97 $\mu\text{g/l}$) in June to a maximum of 5.30 $\mu\text{g/l}$ in July. The monthly average nitrate content was maximum $3.37 \pm 1.68 \mu\text{g/l}$ in S-I and a minimum of $2.26 \pm 1.14 \mu\text{g/l}$ in S-III.

Seasonal fluctuations in nitrate content in sampling stations are shown in Table.3.17. In 2010, during the non monsoon period the minimum nitrate content of $1.18 \pm 0.56 \mu\text{g/l}$ was estimated in S-II; whereas it was maximum ($2.59 \pm 1.57 \mu\text{g/l}$) in S-I. During the southwest monsoon period maximum nitrate content of $2.96 \pm 0.43 \mu\text{g/l}$ in S-II and a minimum of 2.72 ± 1.92 in S- I were noticed. The

northeast monsoon period had a minimum of 2.33 ± 0.94 $\mu\text{g/l}$ in S-III and a maximum of 3.83 ± 2.24 $\mu\text{g/l}$ nitrate in S-I. In 2011, non-monsoon period recorded minimum nitrate content of 1.40 ± 0.68 $\mu\text{g/l}$ in S-II against the maximum of 2.87 ± 1.69 $\mu\text{g/l}$ in S-I. The southwest monsoon period had a minimum of 2.65 ± 1.88 $\mu\text{g/l}$ in S-III and a maximum (2.95 ± 0.17) $\mu\text{g/l}$ in S-II. The northeast monsoon period had a minimum nitrate of 2.45 ± 0.70 $\mu\text{g/l}$ in S-III and a maximum of 4.44 ± 1.32 $\mu\text{g/l}$ in S-I.

Two-way analysis of variance for the data on nitrate content in water samples as a function of variation between stations and seasons were statistically not significant in both the years of study period ($F = 2.35$ and 3.308 ; $F = 4.428$ and 3.496 ; $P > 0.05$) (Table 3.17.a).

Nitrate showed significant positive correlation ($P < 0.05$) with phosphate at S-I and nitrite at S-II. On the other hand it showed a significant negative correlation ($P < 0.05$) with atmospheric and water temperature at S-II and S-III and with phosphate at S-III during 2010. In 2011, nitrate showed a significant positive correlation ($P < 0.05$) with ammonia at S-II and S-III, with phosphate at S-I and with nitrite at S-II. On the other hand it showed significant negative correlation ($P < 0.05$) with sulphate at S-I and S-II, with water temperature and phosphate at S-II and S-III, with carbon dioxide at S-II and with atmospheric temperature at S-III (Tables.3.24 to 3.29).

3.3.15 AMMONIA

The monthly fluctuation and average ammonia content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.31 and 3.32. The ammonia estimated during 2010 ranged from 0.01 mg/l in August to 0.58 mg/l in July, from 0.015 mg/l in August to 0.62 mg/l in June and July and from 0.015 mg/l in August to 0.8 mg/l in December at S- I, S-II and S-III respectively. The monthly average ammonia content was maximum (0.45 ± 0.28 mg/l) in S-III and minimum (0.189 ± 0.1 mg/l) in S-I. In 2011, at S-I the ammonia content varied from a minimum of 0.04 mg/l during February to a maximum of 0.534 mg/l during July. In S-II, the ammonia content ranged from a minimum of 0.04 mg/l in December to a maximum 0.72 mg/l in July. In S-III, it varied from 0.025 mg/l in August to 0.88 mg/l in July. The monthly average ammonia content was maximum (0.20 ± 0.02 mg/l) in S-III against the minimum of 0.172 ± 0.01 mg/l in S-I.

Seasonal fluctuations in ammonia content in sampling stations are provided in Table.3.18. In 2010, during non monsoon period minimum ammonia content of 0.16 ± 0.07 mg/l was estimated in S-I; whereas it was maximum (0.61 ± 0.10 mg/l) in S-III. During southwest monsoon period a minimum of 0.32 ± 0.25 mg/l in S-I and a maximum of 0.45 ± 0.32 mg/l in S- III were noticed. The northeast monsoon period had a minimum of 0.08 ± 0.11 mg/l in S-I mg/l and a maximum of 0.30 ± 0.13 mg/l in S-III. In 2011, during non-monsoon the period minimum ammonia content of 0.049 ± 0.006 mg/l was estimated in S-I against the maximum of 0.189 ± 0.059 mg/l in S-III. The southwest monsoon period had a

minimum of 0.256 ± 0.20 mg/l in S-I and a maximum of 0.29 ± 0.03 mg/l in S-II; whereas the northeast monsoon period had a minimum of 0.144 ± 0.039 mg/l in S-III and a maximum of 0.249 ± 0.164 mg/l in S-II.

The two-way analysis of variance for the data on ammonia content in water samples as a function of variation between stations and seasons were statistically not significant in both the years of study period ($F = 6.119$ and 0.317 ; $F = 4.743$ and 1.109 ; $P > 0.05$) (Table 3.18.a).

In 2010, ammonia was significantly correlated ($P < 0.05$) positively with silicate at S-I and S-II and with manganese and iron at S-III. It showed a significant negative correlation with salinity and zinc at S-I and with dissolved oxygen at S-III. During 2011, it showed a significant positive correlation ($P < 0.05$) with nitrite and copper at S-I and S-II, with nitrate at S-II and S-III and with silicate at S-I. It showed a significant negative correlation ($P < 0.05$) with atmospheric and water temperature, salinity, zinc and iron at S-I and S-II, with electrical conductivity, calcium, magnesium and manganese at S-I and with carbon dioxide and phosphate at S-II (Tables.3.24 to 3.29).

3.3.16 SULPHATE

The monthly fluctuation and average sulphate content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig. 3.33 and 3.34. The sulphate estimated during 2010 ranged from 0.96 ppm in October to 1.8 ppm in March, from 0.1 ppm in December to 2.04 ppm in March and from 1.32 ppm in July to 4.8 ppm in December at stations I, II and III respectively. The monthly average sulphate recorded was high with 2.44 ± 1.0

ppm at S-III and low with 1.28 ± 0.53 ppm in S-II. In 2011, the sulphate content in S-I varied from a minimum of 1.10 ppm during October to a maximum of 1.84 ppm during March. In S-II, the sulphate content ranged from a minimum of 0.18 ppm in December to a maximum of 2.67 ppm in June. In S-III, it varied from minimum of 1.68 in August and maximum of 4.53 ppm in December. The monthly average sulphate recorded was high with 2.58 ± 0.86 ppm at S-III and low with 1.47 ± 0.66 ppm in S- II.

Seasonal fluctuations in sulphate content in sampling stations during the study period are shown in Table.3.19. In 2010, non monsoon season, the mean sulphate content varied from 1.6 ± 0.3 ppm in S-I to 2.13 ± 0.35 ppm in S-III. The southwest monsoon period showed minimum mean sulphate content of 1.24 ± 0.12 ppm in S -I and maximum of 1.8 ± 0.48 ppm in S-III. In northeast monsoon period S- II showed a minimum mean sulphate content of 0.8 ± 0.52 ppm and S- III had a maximum sulphate of 3.38 ± 1.2 ppm. In 2011, during non monsoon period the minimum sulphate content of 1.68 ± 0.18 ppm was estimated in S-I against the maximum of 2.20 ± 0.19 ppm in S-III. The southwest monsoon period had a minimum of 1.60 ± 0.23 ppm in S-I and a maximum of 2.07 ± 0.46 ppm in S- III; whereas the northeast monsoon period had a minimum of 0.75 ± 0.40 ppm in S-II and a maximum of 3.47 ± 0.94 ppm in S-III

The two-way analysis of variance for the data on sulphate content of water samples as a function of variation between stations and seasons were statistically not significant in both the years of study period ($F = 2.952$ and 2.311 ; $F = 0.323$ and 0.023 ; $P > 0.05$) (Table 3.19.a).

Sulphate exhibited a significant positive correlation ($P < 0.05$) with atmospheric and water temperature at S-I and S-II, with salinity, electrical conductivity and calcium at S-I, with carbon dioxide at S-II and with dissolved oxygen, nitrite, manganese, zinc and iron at S-III. It also showed a significant negative correlation ($P < 0.05$) with copper at S-I and S-III, with dissolved oxygen and bicarbonate at S-II and with salinity at S-III during 2010. In 2011, the correlation was significantly positive ($P < 0.05$) with atmospheric temperature at S-I and S-II, with biological oxygen demand at S-I, with water temperature, carbon dioxide and phosphate at S-II and with dissolved oxygen and zinc at S-III. A significant negative correlation ($P < 0.05$) was observed with dissolved oxygen and nitrate at S-I and S-II, with pH and bicarbonate at S-II and with copper at S-III (Tables.3.24 to 3.29).

3.3.17 MANGANESE

The monthly fluctuation and average manganese content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.35 and 3.36. The manganese estimated during 2010 ranged from 0.558 ppm in October to 6.24 ppm in December, from 0.558 ppm in October to 4.26 ppm in December and from 0.5 ppm in July and August to 3.8 ppm in December at stations I, II and III respectively. The monthly average manganese content was maximum 3.27 ± 2.0 ppm in S-I against the minimum of 1.52 ± 1.2 ppm in S-III. In 2011, the manganese content in S-I varied from a minimum of 1.35 ppm during July to a maximum of 6.21 ppm during December. In S-II, the manganese content ranged from a minimum of 1.00 ppm in July to a maximum of 4.50 ppm in

January. In S-III, it varied from 0.47 ppm in July and 4.17 ppm in January. The monthly average manganese content was maximum 3.697 ± 1.62 ppm in S-I and a minimum of 1.65 ± 1.07 ppm in S-III.

Seasonal fluctuations in manganese content in sampling stations are provided in Table 3.20. In 2010, during non monsoon period the minimum manganese content of 2.09 ± 0.91 ppm was estimated in S-III; whereas, it was maximum (4.51 ± 0.78 ppm) in S-I. During southwest monsoon period had a minimum of 0.68 ± 0.29 ppm in S-III and a maximum of 2.02 ± 1.3 ppm in S- I were noticed. The northeast monsoon period had a minimum of 1.79 ± 1.57 ppm in S-III and a maximum of 3.28 ± 0.29 ppm in S-I. In 2011, during non-monsoon period the minimum manganese content of 2.45 ± 1.32 ppm was estimated in S-III and it was maximum (4.53 ± 0.77 ppm) in S-I. The southwest monsoon period had a minimum of 0.95 ± 1.40 ppm in S-III and a maximum 2.51 ± 1.26 ppm in S- I. The northeast monsoon period had a minimum of 1.57 ± 0.89 ppm in S-III and a maximum of $4.05 \pm 0.2.1$ in S-I.

The two-way analysis of variance for the data on manganese content in water samples as a function of variation between stations and seasons were statistically significant in both the years of study period ($F = 21.657$ and 29.566 ; $F = 22.531$ and 19.653 ; $P < 0.01$) (Table 3.20.a).

Manganese showed a significant positive correlation ($P < 0.05$) with zinc and iron at all stations, with salinity and calcium at S-I and with ammonia and sulphate at S-III. On the other hand it showed significant negative correlation ($P < 0.05$) with silicate and copper at all stations during 2010. In 2011 manganese

showed a significant positive correlation ($P < 0.05$) with, zinc and iron at all stations, with salinity and calcium at S-I and with nitrite at S-III. On the other hand it showed significant negative correlation ($P < 0.05$) with silicate and copper at all stations and with nitrite and ammonia at S-I (Tables.3.24 to 3.29).

3.3.18 ZINC

The monthly fluctuation and average zinc content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.37 and 3.38. The zinc estimated during 2010 ranged from 0.406 ppm in August to 0.81 ppm in January, from 0.44 ppm in July to 0.76 ppm in January and December and from 0.32 ppm in April to 0.68ppm in December at stations I, II and III respectively. The monthly average zinc content was maximum (0.58 ± 0.11 ppm) in S-II against the minimum of 0.52 ± 0.09 ppm in S-III. In 2011, zinc content in S-I varied from a minimum of 0.43 ppm during July to a maximum of 0.88 ppm during January. In S-II, the zinc content ranged from a minimum of 0.46 ppm in July to a maximum of 0.85 ppm in January. In S-III, it varied from 0.48 ppm in July to 0.75 ppm in December. The monthly average zinc content was maximum 0.68 ± 0.13 ppm in S-I and it was minimum (0.60 ± 0.09 ppm) in S-III.

Seasonal fluctuations in zinc content in sampling stations during the study period are shown in Table 3.21. In 2010, during non monsoon period the minimum zinc content of 0.47 ± 0.11 ppm was estimated in S-III and it was maximum (0.69 ± 0.09 ppm) in S-I. The southwest monsoon period had a minimum of 0.42 ± 0.02 ppm in S-I and a maximum of 0.49 ± 0.06 ppm in S- III.

The northeast monsoon period had a minimum of 0.59 ± 0.15 ppm in S-I and a maximum of 0.64 ± 0.12 ppm in S-II. In 2011, during non-monsoon period the minimum zinc content of 0.60 ± 0.10 ppm was estimated in S-III; whereas it was maximum (0.78 ± 0.07 ppm) in S-I. During southwest monsoon period a minimum of 0.53 ± 0.04 ppm in S-III and a maximum (0.59 ± 0.09 ppm) in S- II were noticed. The northeast monsoon period had a minimum of 0.66 ± 0.08 ppm in S-III and a maximum of 0.72 ± 0.10 ppm in S-II.

The two-way analysis of variance for the data on zinc content in water samples as a function of variation between stations was statistically not significant in both the years of study ($F = 0.584$ and 3.596 ; $P > 0.05$). But the variation between seasons was statistically not significant in 2010 and statistically significant in 2011 ($F = 3.402$; $P > 0.05$ and $F = 9.133$; $P < 0.05$) (Table 3.21.a).

In 2010, zinc was significantly correlated ($P < 0.05$) positively with manganese at all stations, with iron at S-I and S-II with salinity, calcium and phosphate at S-I and with sulphate at S-III and a significant negative correlation with silicate and copper at all stations, with ammonia at S-I and with atmospheric temperature, water temperature, salinity, and electrical conductivity at S-III. During 2011, it showed a significant positive correlation ($P < 0.05$) with manganese and iron at all stations, with salinity, electrical conductivity and calcium at S-I and with nitrite and sulphate at S-III. It showed significant negative correlation ($P < 0.05$) with silicate and copper at all stations, with nitrite

and ammonia at S-I and S-II and with electrical conductivity at S-III (Tables.3.24 to 3.29).

3.3.19 COPPER

The monthly fluctuation and average copper content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.39 and 3.40. The copper estimated during 2010 ranged from 0.06 ppm in January to 0.43 ppm in August, from 0.08 ppm in February to 0.42 ppm in October and from 0.18 ppm in December to 0.43 in August at stations I, II and III respectively. The monthly average copper content was maximum (0.35 ± 0.085 ppm) in S-III and it was minimum (0.23 ± 0.14 ppm) in S-I. In 2011, copper content in S-1 varied from a minimum of 0.06 ppm during January to a maximum of 0.36 ppm during June. In S-II, the copper content ranged from a minimum of 0.12 ppm in December to a maximum of 0.40 ppm in October. In S-III, it varied from 0.18 ppm in December to 0.42 ppm in July. The monthly average copper content was maximum (0.32 ± 0.07 ppm) in S-III against the minimum of 0.194 ± 0.11 ppm in S-I.

Table 3.22 provides seasonal fluctuations in copper content in sampling stations during the study period. In 2010, during non monsoon period, the minimum copper content of 0.10 ± 0.03 ppm was estimated in S-I and it was maximum (0.31 ± 0.07 ppm) in S-III. The southwest monsoon period had a minimum of 0.34 ± 0.07 ppm in S-I and a maximum of 0.42 ± 0.01 ppm in S- III. Likewise the northeast monsoon period had a minimum of 0.26 ± 0.14 ppm in S-I and a maximum of 0.312 ± 0.10 ppm in S-III. In 2011, during non monsoon period

the minimum copper content of 0.08 ± 0.02 ppm was estimated in S-I; whereas it was maximum (0.29 ± 0.04 ppm) in S-III. The southwest monsoon period had a minimum of 0.28 ± 0.09 ppm in S-I and a maximum of 0.39 ± 0.02 ppm in S-III; whereas the northeast monsoon period had a minimum of 0.22 ± 0.12 ppm in S-I and a maximum of 0.281 ± 0.122 ppm in S-II.

The two-way analysis of variance for the data on copper content in water samples as a function of variation between stations was not statistically significant in both the years of study ($F = 4.239$ and 6.621 ; $P > 0.05$). On the other hand the variation between seasons was statistically significant in 2010 and 2011 ($F = 10.746$ and 9.074 ; $P < 0.05$) (Table 3.22.a).

Copper exhibited a significant positive correlation ($P < 0.05$) with silicate at all stations, with nitrite at S-I and S-II. It also showed a significant negative correlation ($P < 0.05$) with manganese, zinc and iron at all stations, with sulphate at S-I and S-III, with salinity and carbon dioxide at S-I and S-II, electrical conductivity and calcium at S-I and with atmospheric and water temperature at S-II during 2010. In 2011, the correlation was significantly positive ($P < 0.05$) with silicate at all stations and with nitrite and ammonia at S-I and S-II. A significant negative correlation ($P < 0.05$) with manganese, zinc and iron at all stations, with atmospheric temperature, water temperature, salinity, carbon dioxide, electrical conductivity and calcium at S-I and S-II and with nitrite and sulphate at S-III (Tables.3.24 to 3.29).

3.3.20 IRON

The monthly fluctuation and average iron content estimated in the sampling stations during 2010 and 2011 are shown in Tables 3.1 and 3.2; Fig.3.41 and 3.42. The iron estimated during 2010 ranged from 0.96 ppm in May to 2.10 ppm in January, from 1.02 ppm in May to 2.32 ppm in January and from 1.06 ppm in May, August and September to 2.16 ppm in December at S- I, S- II and S- III respectively. The monthly average iron content was maximum (1.55 ± 0.46 ppm) in S-II and it was minimum (1.36 ± 0.38 ppm) in S-I. In 2011, iron content in S-I varied from a minimum of 1.12 ppm during July to a maximum of 2.43 ppm during January. In S-II, the iron content ranged from a minimum of 1.18 ppm in July to a maximum of 2.54 ppm in January. In S-III, it varied from 1.15 ppm in July to 2.25 ppm in December. The monthly average iron content was maximum (1.76 ± 0.48 ppm) in S-II and it was minimum (1.58 ± 0.41 ppm) in S-I.

Seasonal fluctuations in iron content in sampling stations are provided in Table 3.23. In 2010, during non monsoon period the minimum iron content of 1.66 ± 0.41 ppm was estimated in S-I and it was maximum (1.99 ± 0.25 ppm) in S-II. During southwest monsoon period a minimum of 1.08 ± 0.09 ppm in S-I and a maximum of 1.15 ± 0.10 ppm in S- II were noticed. The northeast monsoon period showed a minimum of 1.36 ± 0.36 ppm in S-I and a maximum of 1.55 ± 0.45 ppm in S-III. In 2011, during non monsoon period the minimum iron content of 1.897 ± 0.54 ppm was estimated in S-I; whereas it was maximum (2.21 ± 0.26 ppm) in S-II. The southwest monsoon period had a minimum of 1.30 ± 0.17 ppm in S-I

and a maximum of 1.42 ± 0.31 ppm in S- II. The northeast monsoon period had a minimum of 1.52 ± 0.29 ppm in S-I and a maximum of 1.66 ± 0.44 ppm in S-III.

The two-way analysis of variance for the data on iron content in water samples as a function of variation between stations was not statistically significant in 2010 and 2011 ($F = 4.49$ and 3.277 ; $P > 0.05$). But the variation between seasons was statistically highly significant in 2010 ($F = 63.60$; $P < 0.001$) and more significant in 2011 ($F = 42.767$; $P < 0.01$) (Table 3.23.a).

The iron showed a significant positive correlation ($P < 0.05$) with manganese at all stations, with zinc at S-I and S-II, phosphate at S-I, salinity and carbon dioxide at S-II and with ammonia and sulphate at S-III. On the other hand it showed significant negative correlation ($P < 0.05$) with silicate and copper at all stations and with magnesium at S-III during 2010. In 2011, the correlation was significantly positive ($P < 0.05$) with manganese and zinc at all stations, atmospheric temperature, water temperature, salinity and electrical conductivity at S-II and with nitrite at S-III. It showed a significant negative correlation ($P < 0.05$) with silicate and copper at all stations and with nitrite and ammonia at S-I and S-II (Tables.3.24 to 3.29).

3.4. DISCUSSION

The temperature is one of the important physical factors, which affects the chemical and biological reactions in water. It regulates the rate of photosynthesis in aquatic ecosystem. The temperature variation is one of the factors in the swamp and estuarine system, which may influence the physicochemical characteristics and also influence the distribution and abundance of fauna and flora (Soundarapandian *et al.*, 2009). Atmospheric temperature recorded during the study period showed seasonal variations at all stations. In general non monsoon season recorded higher temperature compared to the monsoon season. In the present study, a minimum atmospheric temperature was recorded during northeast monsoon and a maximum was noticed during non monsoon period. The maximum atmospheric temperature was recorded during the summer season owing to the clear sky with more solar radiation. Less solar radiation with cloudy sky and more rainfall during the monsoon season greatly reduced the air temperature (Sampathkumar and Kannan (1998) and Karuppasamy *et al.* (1999). Similar condition was also noted by Mohideen Askar Nawas (2009) in Raiakkamangalam estuary; Palpandi (2011) in velar estuary and Srilatha *et al.* (2012) in Muthupettai mangrove. The intensity of solar radiation, bathymetry of the environment, tides and variation in atmospheric temperature influence the temperature variations in estuaries and coastal waters (Borrego and Borrego, 1982). Atmospheric temperature has a significant positive correlation with water temperature, salinity carbon dioxide, biological oxygen demand, sulphate and iron and a negative correlation with dissolved oxygen, nitrite, nitrate, copper, magnesium and zinc at selected sampling stations of the estuarine environment.

Generally, surface water temperature is influenced by the intensity of solar radiation, evaporation, insulation, freshwater influx and cooling and mix up with ebb and flow from adjoining neritic waters (Govindasamy *et al.*, 2000). Desai (1995) suggested that the water temperature may depend on the season, geographic location and sampling time. In the present study July and August in 2010 and July and November in 2011 showed a low water temperature. During the monsoon period, the water temperature was low when compared with non monsoon period, but this variation was not much noticeable in between stations. These values were within the acceptable levels for survival, metabolism and physiology of aquatic organisms. Water temperature has some positive and negative effects on plant growth. The most suitable water temperature for plant growth is 20-35 °C; temperature over 30 °C can cause regression in growth and decay in plants (Lawson, 2011). Sukumaran (2002) in the Manakudy estuary and Regini Bala Singh (2004) in Rajakkamangalam, Kadiapattinam and Manakkudy estuary reported a premonsoon maximum and post monsoon minimum in surface water temperature. Higher water temperature during the summer season could be due to the meteorological characteristics, shallowness of the estuary and its proximity to land, resulting in rapid changes in temperature in accordance with the changes in atmospheric temperature (Karunagaran, 1990). Summer peaks and monsoonal low water temperature were noticed by several workers in the west coast of India (Saravanakumar *et al.*, 2008). During the study period, the difference between the highest and lowest temperature of surface water were much lower than 8 °C. These values are very much comparable with values recorded at most of the Indian estuaries where the difference between the highest

and lowest values never exceeded 8 °C to 10°C (Chandran and Ramamoorthi, 1984a; Gouda and Panigrahy, 1993). During March and April the water temperature was found to be higher due to clear sky, more solar radiation and higher atmospheric temperature. The bar mouth remained closed during this period and the flow was minimum and due to these conditions, the temperature remained higher. Jagadeesan (1986) observed maximum water temperature during summer months and minimum during monsoon months in Coleroon estuary. Water temperature shows a significant positive correlation with atmospheric temperature, carbon dioxide, electrical conductivity, calcium, salinity, sulphate and bicarbonate at selected sampling stations.

In the present study water temperature was positively ($P < 0.05$) correlated with atmospheric temperature at all stations. Similar findings have also been reported by Rama Sarma (1965) in Godavaari estuary, Varma *et al.* (1975) in Mondovi estuary, Vijayalakshmi and Venugopalan (1973), Sivakumar (1982) and Chandran and Ramamoorthi (1984 a) in Vellar estuary, Mishra *et al.* (1993) in Bahuda river estuary and Sharma (1980) and Jeyasingh (1997) in reservoirs. Hence it can be inferred that the temperature variations of the present sampling stations are mainly governed by the atmospheric variations as was earlier observed in other coastal bodies of water (Qasim *et al.*, 1969; Patra 1990; Gouda and Panigrahy 1993; Sukumaran, 2002; Kumaraswamy, 2005 and Mohideen Askar Nawas, 2009).

Hydrogen ion concentration (pH) is the master that controls all aquatic chemical and biological processes. The pH of natural waters affects biological

and chemical reactions control the solubility of metal ions and affect natural aquatic life. The seasonal variations in pH were mainly affected by temperature, carbonate and bicarbonate system, rather than the photosynthetic activity of the primary producers (Abdo, 2005). pH did not show any marked variations during the study period, but decrease in pH was recorded in the month of January. Monthly mean data showed a slightly acidic pH in all the selected stations. Streams and rivers transporting large quantities of humic material in colloidal suspension are frequently slightly acidic. Anila Kumary *et al.* (2007) recorded acidic pH during the monsoon season in Adimalathura estuary. Sreenivasan and Pillai (1972) stated that the high buffering of water is responsible for the very little change in pH in the Pulicat Lake. In the present study very low pH was recorded in the month of January in S-II and S- III this may be due to the discharge of sewage into the water body from nearby villages and mixing of coconut retting effluent. pH of water at sewage discharge points were usually lower than that of the river water (Sharma, 1980). Low pH value was also recorded by Abdul Azis (1978) in the retting grounds of the backwaters of Kerala, Bijoy Nandan (1991) in Kadinamkulam Kayal and Shibu (1991) in Paravar Lake and Shruthi *et al.* (2011) in Gangoli estuaries. The mixing of ret liquor in water bodies causes health hazards to the human beings and the distribution of flora and fauna. In 2010, season wise data showed maximum pH during the northeast monsoon and minimum during southwest monsoon and non monsoon. High pH in monsoon was reported by Subramanian (1982) in Krishna river estuary and Gouda and Panigrahy (1993) in Rushikulya estuary. The reduction in phytoplankton density in monsoon may bring about a sharp decline

in pH (Evangeline, 1975). Upadhyay (1988) reported low values of pH during monsoon in the Mahanadi estuarine system. Low pH recorded in the present study during southwest monsoon may be due to the reduction of phytoplankton density. In the year 2011, minimum pH was noticed in non monsoon period and maximum in northeast monsoon. Similar findings were reported by Prema (2002); and Selvamohan (2006). Monsoon influenced pH variation was observed by Palanichamy and Rajendran (2000) from Palk Bay, Prabu *et al.* (2008) from Pichavaram mangroves, Damotharan *et al.* (2010) from Point Calimere coastal waters. The pH of river water entering estuaries is high during dry season and decreases markedly during monsoon. During dry season, the river flow is governed by the seasonal water pH, which would depend on the type of strata through which it flows. On the other hand, the river flow during monsoon is dominated by the rainwater, which generally has lower pH (Ravaniah *et al.*, 2010). pH has direct or indirect effects on photosynthesis and growth of water plants. High pH causes more carbonate and bicarbonate in water (Lawson, 2011). pH has a positive significant correlation with dissolved oxygen in this study.

In the present study, December 2010 and April 2011 showed increase in salinity and lowest values were recorded in June, October and November. Salinity distribution in the estuaries is mainly influenced by the opening and closing of the bar mouth of the estuary. Variation is also caused by rainfall and freshwater discharge (Nair *et al.*, 1984). Salinity is one of the important factors which profoundly influence the abundance and distribution of the animals in estuarine environment. Salinity in all the stations was high during the summer

season and low during monsoon season. The maximum salinity recorded during summer season was due to the high degree of evaporation of surface water and decreased freshwater inflow and land drainage. Similar observations were also made by Das *et al.* (1997) in Mahanadi estuary. The minimum salinity during monsoon season was due to the monsoonal rain, flooding and fresh water input into the study areas. During the study period, it has been observed that S-1 has recorded more salinity compared to S- II and S-III, since; it is situated near to the estuarine mouth, adjacent to the Arabian Sea. Low salinity recorded during southwest monsoon was due to heavy rainfall and large quantity of freshwater inflow. Salinity recorded during the study period was higher during non monsoon that is due to low rainfall, decreased fresh water inflow, land drainage and rise in temperature. Maximum salinity values in summer and minimum during monsoon were also observed from Vellar estuary (Palpandi, 2011), Cuddalore Uppanar water (Mathevan Pillai, 1994), Pondicherry coast (Ananthan, 1995), Coastal waters of Kalpakkam (Satpathy, 1996) and Muthupettai mangrove (Srilatha *et al.*, 2012). High salinity recorded in S- I and S-II in December may be attributed to the inflow from the sea and also from nearby rivers. Lawson (2011) reported that rainfall could cause dilution of estuaries and hence cause reduction in salinity, while heat generated by sunlight in dry season months would cause evaporation of the surface water making it saltier and hence more saline. In this study salinity has a significant positive correlation with atmospheric temperature, water temperature, carbon dioxide, electrical conductivity, calcium, and magnesium and negatively correlated with dissolved oxygen at selected sampling stations

were observed which is in agreement with the report of Mohideen Askar Nawas (2009).

Dissolved oxygen is a regulator of metabolic activities of organisms and thus governs metabolism of the biological community as a whole and also acts as an indicator of trophic status of the water body (Saksena and Kaushik, 1994). During the study period wide range of variations in the concentration of dissolved oxygen were observed. Similar variations were also reported by Mishra *et al.* (1993) in Bahuda estuary. Dissolved oxygen varies according to many factors; the main factors are due to photosynthesis and respiration by plants and animals in water. The temperature and salinity affect the dissolution of oxygen (Saravanakumar *et al.*, 2008). In the present investigation, higher values of dissolved oxygen were recorded during northeast monsoon season and low values during non monsoon season. The high values during monsoon might be due to the cumulative effect of higher wind velocity coupled with heavy rainfall and the resultant freshwater mixing as reported by Sukumaran (2002) and Regini Bala Singh (2004) in Manakudy estuary. Similar observations were also made by Saravanakumar *et al.*, 2008; Damotharan *et al.*, 2010 and Palpandi, 2011). Paramasivam and Kannan (2005) attributed that seasonal variation of dissolved oxygen is mainly due to freshwater flow and terrigenous impact of sediments. Egborge (1971) reported that dissolved oxygen is generally higher in the wet season in the tropics. Oxygen is generally reduced in the water due to respiration of biota, decomposition of organic matter, rise in temperature, oxygen demanding wastes and inorganic reductant such as hydrogen sulphide, ammonia, nitrites, ferrous iron, etc. (Sahu *et al.*, 2000). Introduction of organic wastes and its

decomposition in the water can be the reason for the low concentration of oxygen at S-III compared to other stations. The low value of dissolved oxygen in summer may also be due to microbial demand for oxygen in the decomposition of suspended organic matter as reported by (Palharya and Malvia, 1998; Umayorubhagan *et al.*, 1998; Prasathan and Vasudevan Nair, 2000). Similar findings were also reported by Ghosh and Basu (1968), Bijoy Nandan and Abdul Azis (1990). Insufficient dissolved oxygen in the water column causes the anaerobic decomposition of any organic material present, which tends to cause the formation of noxious gases such as hydrogen sulphide and development of carbon dioxide and methane in the sediments, which bubble to the surface or tend to float on the settled sludge as mat, which are decomposed of various organic materials (Karunagaran, 1990 and Ravaniah *et al.*, 2010). Dissolved oxygen has a significant positive correlation with bicarbonate and nitrite and negative correlation with atmospheric temperature, water temperature, salinity, carbon dioxide, electrical conductivity and sulphate at selected sampling stations. A negative correlation of dissolved oxygen with salinity and temperature was reported by Dye (1978), Jeyasingh (1997), Subramanian and Mahadevan (1999), Prema (2000) and Sukumaran (2002). Jeyasingh (1997) reported a positive correlation of dissolved oxygen with nitrite, nitrate and silicate content.

The pH, alkalinity and free carbon dioxide are interrelated in aquatic ecosystems. Most of the free carbon dioxide in water comes from the decomposition of organic matter and from respiration of organisms (Singh, 1999). Its increased levels may affect the pH of the water (Kotpal and Bali, 1989). In the present investigation S- II and S-III showed high carbon dioxide

content compared to S- I. Decomposition of organic matter was the main reason for the high concentration of carbon dioxide in these zones. The decomposition of organic matter in the sediment, domestic sewage and industrial effluents causes an increase in carbon dioxide concentration (Shrihari and Venkatesha, 1994). High concentration of carbon dioxide was reported during nonmonsoon period when the mouth of the estuary was closed. During this period, the sea- estuary interaction came to a standstill leading to the development of a stagnant condition in the estuary and the canal. Similar observation was also reported by Umayorubhagan *et al.* (1998). In the present study carbon dioxide showed a significant positive correlation with atmospheric and water temperature, salinity, biological oxygen demand and calcium at selected sampling stations.

The biological oxygen demand observed in S-II and S-III were higher than S-I. Biological oxygen demand reveals the content of microorganisms present in the water under investigation and its organic matter load. The rate of oxygen consumption in an estuary is affected by a number of variables, including temperature, the presence of certain kinds of microorganisms and the type of organic and inorganic material in the water. Biological oxygen demand directly affects the amount of dissolved oxygen in estuaries. Low values of biological oxygen demand were observed in S-I indicate the absence of organic pollution. Vareethiah and Haniffa (1998) reported minimum biological oxygen demand levels during monsoon due to the entry of floods. In the present investigation S-II showed maximum biological oxygen demand in non monsoon season and was due to the mixing of retting effluent. In S-III high biological oxygen demand was reported during monsoon and non monsoon period due to the mixing of domestic

waste from nearby villages and retting effluents. Karthikeyan *et al.* (2004) observed that the maximum biological oxygen demand value during non monsoon season was due to the consumption of oxygen for the oxidation of the large amount of sewage water and the minimum value in monsoon was due to the high oxygen in Uppanar estuary. Similar observation was made by Ananthan (1995) in Pondicheery coast. The occurrence of high biological oxygen demand content in polluted zone was reported by various workers like Abdul Azis (1978), Murugan and Ayyakkaannu (1991), Jameel (1998), Panigrahy *et al.* (1999) and Fokmare and Musaddiq (2002). The higher value of biological oxygen demand during summer could be attributed to higher bacterial activity under high temperature. Its lower value during winter might be due to retarded bacterial activity under decreased light intensity and lowered temperature (Prabhakar *et al.*, 2011). In the present study BOD showed a positive correlation with carbon dioxide in S-II, which is in agreement with the report of Prema (2000) and Mohideen Askar Nawas (2009)

In S-I, maximum bicarbonate content was observed in non monsoon and minimum in monsoon season. During monsoon fertilizers and like materials from the surrounding coconut and areca nut gardens and paddy fields, accumulate in the estuarine environments and subsequent drying during non monsoon might have contributed to the highest alkalinity. At high temperature carbonate may be precipitated out in the form of bicarbonate (Hutchinson, 1957). Higher alkalinity favors the growth of phytoplankton. Trivedi and Goel (1992) pointed out that dilution plays an important role in lowering the alkalinity of water. Shrivastava and Patil (2002) suggested that the alkalinity is directly related to the abundance

of phytoplankton which dissociates bicarbonate into carbonates and carbon dioxide. The carbon dioxide, thus, released is used in photosynthesis. George *et al.* (1966) and Ravaniah *et al.* (2010) have opined that with a pH range of 7.0 to 9.0 in water bodies, the bicarbonates concentration remains high. In the sampling stations, S-II and S-III the maximum values of bicarbonate were recorded during the monsoon seasons against minimum values during nonmonsoon season. Similar observations were earlier made by Prema (2000) and Mohideen Askar Nawas (2009). Padma and Periakali (1999) reported that the increase in alkalinity was due to the input of fresh water and dissolution of calcium ion from the sediment, which increased the carbonate and bicarbonate concentrations. Wide range of alkalinity was reported by Agarkar and Garode (2000) and Regini Bala singh (2004). Bicarbonate showed a positive significant correlation ($P < 0.05$) with electrical conductivity, magnesium and calcium in selected sampling stations.

Electrical conductivity is a measure of capacity of a substance or solution to conduct electric current. Solutions of most inorganic compounds and more abundant ions have higher conductivity (APHA, 1985). Electrical conductivity is a good measure of dissolved solids. Conductivity is a measurement used to determine mineralization and determining amounts of chemical reagents or treatment chemicals to be added to the water (Pravin Singare *et al.*, 2011). The electrical conductivity shows seasonal variation with respect to different sampling station. It depends on the amount of dissolved solids in water. In this study, high electrical conductivity is noticed during non monsoon season. But in S-III high value of electrical conductivity is also recorded during southwest

monsoon season. Singh and Sharma (1986) reported that during non monsoon months electrical conductivity showed an increasing trend with increase in temperature. Francis Andrade *et al.* (2011) also observed high electrical conductivity during pre-monsoon season. The low mean electrical conductivity value recorded during rainy season may be due to water dilution, while the higher electrical conductivity recorded in dry season may be attributed to reduced water volume and high rate of evaporation (Tukura *et al.*, 2012). Manikannan *et al.* (2011) also noted high electrical conductivity values during summer and lower during monsoon. Similar observations were also recorded during the study period. But Phiri *et al.* (2005) reported high values during rainy season than summer seasons. The higher values in the rainy season could be due to ground water and surface runoff from the surrounding farming areas that might have brought into ionic substances from fertilizers. Selvamohan (2006) reported that electrical conductivity was high during northeast monsoon in the bar mouth of the experimental estuary and lower during non monsoon at fresh water zone. Precipitation removes ions, which contribute to the conductivity of water. Electrical conductivity is the net result of many hydrodynamic factors, including tides, rainfall, freshwater and groundwater inputs (Dikou Angela and Triantaphyllou Nikos, 2008). Electrical conductivity exhibited a significant positive correlation ($P < 0.05$) with salinity, calcium and magnesium in selected sampling stations. Mohideen Askar Nawas (2009) also reported a significant positive correlation ($P < 0.05$) of electrical conductivity with magnesium.

The calcium is one of the most abundant substances of natural water being present in high quantities in the rocks. Udhaya Kumar *et al.* (2006)

reported that the hardness of water is due to excessive presence of calcium and magnesium. Calcium and magnesium play an important role in antagonizing the toxic effect of various ions and neutralizing the excess acid produced (Das and Srivastava, 2003). In the present study high calcium content was reported in S- II and S-III which may be due to the addition of sewage, detergents and retting effluent. Mohanta and Patra (2000) suggested that addition of sewage, detergents and large scale human use might be the cause of increasing hardness in river water. S-I recorded high values during non monsoon and low values in monsoon but in S- II and S- III recorded high values in monsoon season. Lowering of calcium values during monsoon season is due to dilution by fresh water inflow caused by rain. Naik (1978) observed that decline of calcium level in the near shore waters of Goa during monsoon months was due to dilution effect. High concentration in the following seasons appeared to be largely due to recovery of calcium for gradual attainment of normal estuarine conditions. High values recorded in S-II and S-III during monsoon may be due to high discharge of sewage and retting effluents. The calcium content was high in Arabian Sea and Mandovi and Zuari estuaries (Sen Gupta and Sugandhini, 1981), west coast of India (Sugandhini and Dias, 1982) and Vellar estuary (Palanichamy and Balasubramanian, 1989). Calcium and magnesium are two major elements occurring normally, among eleven ions of seawater and are considered as 'major constituents', which are leached into the aquatic system by weathering process. In coastal waters comprising near shore, the concentration of these two ions varies with the factors such as land drainage, precipitation and dissolution. These

characteristics could also be pertinent to the shallow aquatic system besides the biological uptake (Ravaniah *et al.* 2010 and Lawson, 2011).

All kinds of natural waters contain magnesium. Magnesium is essential for chlorophyll growth and acts as a limiting factor for the growth of phytoplankton (Dagaonkar and Saksena, 1992). Therefore depletion of magnesium reduces phytoplankton population. Lower concentration of magnesium is observed during northeast monsoon season. The decline in Ca^{++} and Mg^{++} due to rainfall may affect the utilization of planktonic organisms (Bhatt and Pathak, 1992). In the present study high values of magnesium were recorded during non monsoon and low values during monsoon months. Calcium and magnesium showed positive as well as negative correlation with tested water quality parameters at selected sampling stations of the estuary.

Nutrients are considered as one of the most important parameters in the estuarine environment influencing growth, reproduction and metabolic activities of living beings. According to Satpathy *et al.* (2010), the distribution and behavior of nutrients in the coastal environment exhibit considerable variations due to rainfall, quantum of fresh water inflow, tidal incursion and also biological activities.

The major source of dissolved silica is the weathering of rocks and mineral in the catchments area. Silicate is an essential nutrient for growth of diatoms that are important food to fishes (Nath and Srivastava, 2001; Johnson, 2004). In the present study silicate content was found to be higher than that of the other nutrients and was high during southwest monsoon and low during non

monsoon season. High silicate content recorded during monsoon season may be due to rain fall and land runoff. During monsoon, the main sources of silicate are land runoff and precipitation (Qasim and Sengupta, 1981; Nair *et al.*1983a; Mathavan Pillai.1994). The high monsoon values could be due to large influx of fresh water derived from land drainage carrying silicate leached out from rocks and also from the bottom sediment (Govindasamy *et al.*, 2000 and Shruthi *et al.*, 2011). The low values recorded in the summer could be attributed to uptake of silicates by phytoplankton for their biological activity (Saravanakumar *et al.*, 2008). The dissolution of particulate silicon carried by the river, the removal of soluble silicates by adsorption and co-precipitation of soluble silicon with humic compounds and iron are some of the processes which might have caused the depletion of silicate in summer months (Rajasegar, 2003). Sukumaran (2002) reported that low concentration of silicate was due to reduction in fresh water input, higher temperature and salinity and removal of biological processes.(Sushanth and Rajashekhar,2012) also recorded high values of silica during monsoon and lowest during post monsoon season in coastal waters of Uttara Kannada district.

Major sources of phosphate in water are domestic sewage, agriculture effluents and industrial waste waters. The high concentration of phosphate is, therefore, indicative of pollution. In the present study, high values were recorded during December in S-I but S-II and S-III in the month of June. High values of inorganic phosphate may be attributed to the runoff from the land during monsoon, domestic sewage and agricultural effluents. The addition of super phosphates applied in the agricultural fields as fertilizers and alkyl phosphates

used in households as detergents can be other sources of inorganic phosphates during the season (Senthilkumar *et al.*, 2002; Ajithkumar *et al.*, 2006). High monsoonal value may be due to heavy rainfall, land runoff, its autochthonous origin and weathering of rocks liberating soluble alkali metal phosphates, the bulk of which are carried into the estuaries (Govindasamy *et al.*, 2000). The variations may also be due to the processes like adsorption and desorption of phosphates and buffering action of sediment under varying environmental conditions (Rajasegar, 2003). Seasonally pooled data showed high values during northeast monsoon in S-I but in S-II and S-III high values were observed during non monsoon season. The high values recorded during non monsoon in S-II and S-III may be due to the mixing of domestic sewage and detergents from nearby villages. High phosphate during monsoon period was observed by (Prasanna and Ranjan, 2010) in Dhamra Estuary. High values of phosphate throughout the year were observed by Ragothman and Patel (1995) in the Narmada estuary. Phosphate concentration in the coastal waters depends upon its concentration in the fresh water that mixed with the seawater within the land-sea interaction zone, phytoplankton uptake, addition through localized upwelling, and replenishment as a result of microbial decomposition of organic matter (Satpathy *et al.*, 2010).

The main source of nitrogen in the estuary is the river which carries nitrogen in the form of detritus during rainy seasons derived from plants and animals (Ramadhas, 1977 and Chandran and Ramamurthy, 1984b). Inorganic nitrogen is present in an aquatic biosphere as oxidized nitrite, nitrate and also as reduced ammonia. In the present study dissolved nitrite concentration was lower than the nitrate. Since nitrite is an unstable form, its oxidation into nitrate can be

considered as the main reason for the low nitrite. Maximum nitrite content was recorded in southwest monsoon season and minimum values were recorded during non monsoon. Maximum nitrite was obtained in S-II and minimum in S-I and S-III. Very low concentration observed in S-III may be due to sewage input and organic pollution as made by Nair *et al.* (1984) in the Astamudi estuary. Nitrite is an unstable form its oxidation into nitrate can be considered as the main reason for the observed low nitrite content (Tara Devi, 2002) in Manakudy estuary. The higher values of nitrite observed during monsoon was mainly caused by the heavy river runoff. The increase in concentration of nitrite recorded during monsoon season could be due to variation in phytoplankton excretion, oxidation of ammonia and reduction of nitrate and by recycling of nitrogen and bacterial decomposition of planktonic detritus (Asha and Diwakar, 2007) and also due to denitrification and air-sea interaction exchange of chemicals (Mathew and Pillai, 1990; Choudhury and Panigrahy, 1991; Rajasegar, 2003). The low nitrite reported during non monsoon may be due to less fresh water input, higher salinity and uptake by phytoplankton. The same was recorded by Sivakumar (1982) from Vellar estuary and by Edward and Ayyakannu (1991) from Kolhdarn estuary. In the present study nitrite showed a positive correlation with dissolved oxygen, nitrate and silicate, which is in agreement with the report of Prema (2000) and Sukumaran (2002).

The nitrate is an essential nutrient but at higher concentration it becomes toxic and is capable of disturbing the aquatic environment but nitrate level less than 0.5 ml/l will not pollute the water (Ayoola and Kuton, 2009). In the present study maximum values were obtained during northeast monsoon period in S-I

while in S-II and S-III high values were recorded during southwest monsoon. The nitrate concentration suddenly increased with the onset of monsoon along the estuary, which could be attributed to heavy land drainage, Such an increase in concentration of nitrate was also reported by Qasim and Sengupta (1981), Chandran and Ramamoorthi (1984b) and Govindasawamy *et al.* (2012). The high values recorded during monsoon season may be mainly due to higher rate of regeneration from organic materials as reported by (Prema, 2000). Wolfhard and Reinhard (1998), who concluded that nitrates are usually built up during dry seasons and that high level of nitrates, are only observed during early rainy seasons. High concentration of nitrate registered during monsoon season might be due to heavy rainfall, resultant river runoff, land drainage and input of fertilizers from the adjacent agricultural fields and oxidation of ammonia (Anbazhagan, 1988; Prasanna and Ranjan, 2010 and Tukura *et al.*, 2012). The low values recorded during non monsoon period may be due to its utilization by phytoplankton. Similar observations were also made by Gouda and Panigrahy, 1995; Das *et al.*, 1997 and Govindasamy *et al.*, 2000. Sewage contamination of the estuary attributes to comparatively high values of nitrate in Poonthura estuary (Anila Kumary and Abdul Azis, 1992). Maximum value of nitrate in monsoon and minimum in summer season were also recorded by Qasim *et al.*(1969) from Cochin backwaters, De Souza (1977) from Mandovi and Zuari estuaries, Sivakumar (1982) in Vellar estuary, Hari Muraleedharan *et al.* (2010) in Thondi coastal waters and Sundaramanikam *et al.* (2008) in Parangipettai and Cuddalore coast. In the present study nitrate showed both positive and negative correlation

with other tested water quality parameters. Gouda (1996) and Panigrahy *et al.* (1999) reported negative correlation between nitrate and salinity.

The presence of ammonia is an evidence of sewage inflow to a water body and free ammonia serves as an indicator of aquatic pollution (Nath and Srivastava, 2001). In the present study also S-III, reported maximum ammonia than other two stations due to the discharge of domestic sewage from nearby houses. It was higher during rainy season compared to summer. This was mainly caused by the rainfall and the resulting river run off carrying large amount of detritus which increase the ammonia content during these seasons. High concentration of ammonia may be due to the death and subsequent decomposition of phytoplankton and also might be the excretion of ammonia by planktonic organisms (Segar and Hariharan 1989; Ananthan, 1995; Rajasegar, 1998). Lower concentrations of ammonia were recorded during the non monsoon season. In the present study, ammonia exhibited both positive and negative correlation with other tested water quality parameters.

The sulphate ion is one of the major anions occurring in natural waters. Many sulphate compounds are readily soluble in water. Most of them originate from the oxidation of sulphite ores, presence of shales and the solution of gypsum and anhydrite. In the absence of dissolved oxygen, nitrate and sulphates serve as a source of oxygen for biochemical oxidation produced by anaerobic bacteria. Under anaerobic conditions, sulphate ion is reduced to sulphide ion, which establishes equilibrium with hydrogen ion to form hydrogen sulphide. The presence of hydrogen sulphide leads to corrosion of pipes (Sawyer *et al.*, 2000).

In this investigation, sulphate is high during non monsoon and low during monsoon season. Low sulphate in monsoon could be due to the dilution effect while high values in summer may be due to leaching from catchments (Mitra, 1998). In the present study S-III recorded high sulphate during northeast monsoon, this may be due to decomposition of sulphide bearing minerals and sulphate rich effluents from husk retting grounds. The sulphate content exhibited both positive and negative correlation with other tested water quality parameters.

Variation in metal concentrations is due to the presence of major sources of metal pollution, intensive human activity and discharge of municipal waste and industrial effluents (Govindasamy and Azariah, 1999). Martin Deva Prasath and Hidayathulla Khan (2008) reported that the variation in the metal concentration is due to the impact of tsunami that caused large scale seawater inundation and the receding tidal waves carried into the sea, debris, anthropogenic wastes adjacent terrestrial parts including plastic materials and domestic disposals from the near lands. Trace elements in estuary were also affected by colloid destabilization and precipitation, biological uptake and benthic inputs (Huang and You, 2007). Padmini and Vijaya Geetha (2007) observed higher concentrations of metals during summer than the monsoon in Ennore estuary. In the summer seasons, when the fresh water inflow in the estuary is largely anoxic, dissolved metal concentrations tend to be very low and the metal partitioning in those conditions favours adsorption to suspended particles and the sediments (Mubiana *et al.*, 2005). The increase of heavy metal concentration may be due to multiple source of pollution such as sewage, pesticides, industrial waste, etc (Hassan *et al.*, 2010). During monsoon the heavy

metal concentrations measured were high when compared with post-monsoon, summer and pre-monsoon (Rajkumar *et al.*, 2011).

In this study high manganese concentration was reported during non monsoon season and low during southwest monsoon season in 2010. In 2011 also high values were observed during non monsoon in S-I and S-III but in S-II high values were observed during northeast monsoon season and low manganese content was reported in southwest monsoon in all the sampling stations. Ruo-Mei Wang *et al.* (2009) observed higher dissolved manganese concentration in the dry season compared to the wet months in the Gaoping estuary. Sources of dissolved manganese in water columns include bacterial reduction of Fe–Mn oxides, anthropogenic contribution, and benthic sources and desorption from re-suspended particles. The removal process of manganese, however, can be affected by desorption and flocculation of suspended particles (Colbert and Mc Manus, 2005; Huang and You, 2007). Murthy and Rao (1987) observed high metal concentrations during summer are due to evaporation. Caccia and Millero (2003) also observed high metal concentration during summer and low concentration during winter. The higher concentration of metals observed during monsoon could be attributed to the heavy rainfall and subsequent river runoff, bringing much industrial and land derived materials along with domestic, municipal and agricultural wastes, which include residues of heavy metal containing pesticides (Pragatheeswaran *et al.*, 1986; Senthilnathan and Balasubramanian, 1997; Ananthan *et al.*, 1992, 2005; Karthikeyan *et al.*, 2007). Manganese has a positive significant correlation value with zinc and iron in the selected sampling stations.

Zinc is naturally present in water. High concentration of zinc was noticed during non monsoon season in S-I but in S-II and S-III its concentration increases during northeast monsoon period. Higher concentrations of zinc during the monsoon season at S-II and S-III could be attributed to the heavy rainfall and the subsequent freshwater input bringing much land derived materials along with domestic, municipal and agricultural wastes. Similar observations were reported earlier by Anbazhagan (1988) and Sampathkumar (1992). High concentration of zinc may be due to more discharge of zinc containing fertilizers, pesticide through the river. Zinc has a positive significant correlation value with manganese and iron in the selected sampling stations.

During this study period, copper content was also high during southwest monsoon and low during non monsoon. Pragaswari *et al.* (1986) reported an increase in the concentration of copper during the monsoon period in Vellar estuary. Low values of copper during pre monsoon indicated a low terrestrial supply of copper from agricultural fields (Venugopal *et al.*, 1982). Govindasamy *et al.* (1997) reported high concentration of copper in the Pondicherry coast during monsoon season and suggested that it may be due to the differences in the sources of heavy metal to the aquatic biotopes. The maximum copper observed in the water samples of the Thengapattinam estuary was far below the maximum allowable concentration of copper (1ppm). In Ennore estuary, Rajathy and Azariah (1996) reported that the lesser values of copper in the estuary may be due to the biological utilization of copper by the aquatic organism and supported by Lee (1970) who reported that the differential profile of copper, is suggestive of selectivity in absorption or due to secondary mobilization of metals by organic

substances. The concentration of dissolved trace metals gradually decreased towards the lower reaches of the estuary may be, due to the salinity-induced solubilization of the particulates associated matter Duinker and Kramer, (1977). Rantala and Loring (1985) substantiate the decrease in copper concentrations with increasing salinity levels. In this study higher concentration of copper was reported in S-II and S-III may be due to dumping of domestic and municipal waste and agricultural run-off from nearby areas. (Srinivasa *et al.*, 2007) reported that heavy metals are introduced into the aquatic environment by dumping domestic and municipal wastes, industrial effluents, urban runoff, agricultural run-off, atmospheric deposition and mining activities. Domestic waste water is the major anthropogenic source of copper in waterways (Isaac *et al.*, 1997 and Nriagu and Pacyna 1988). The dissolved labile copper concentrations were also high both at the surface and in bottom waters of the Mandovi estuary in the river mouth (George *et al.*, 1984). Copper has a significant negative correlation ($P < 0.05$) with manganese, zinc and iron at all stations.

Iron is the most important transition element and is also the most well known metal in biological systems. Its presence in water originates from rock dissolution and minerals, as well as steel production and other industrial wastewater (Galvin, 1996). Iron content recorded in the study period may be due to the sewage disposal. Ouseph (1992) stated that high concentrations of trace metals in the Cochin backwaters may be due to the anthropogenic input, discharge of effluents from the local industries and sewage disposal. Trace metal concentration varies with respect to time as well as location (Sankaranarayanan *et al.*, 1998). Among the three stations higher concentration was recorded at S- II.

Such spatial variations could be due to difference in the source of heavy metals to the aquatic biotopes such as variable metal inputs into the aquatic environs, seasonal fluctuations in micro phytoplankton cell mass related to productivity and change in the physical, chemical and biological characteristics of the surrounding water (Chan, 1989). Iron shows a significant positive correlation with manganese and zinc at selected sampling stations.