

A Seasonal Evaluation of Dynamics of an Aquatic Ecosystem, Kochi, Kerala, India

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Abstract

Studies on the hydrological features of the marine and estuarine environment is of great importance since the general distribution, migration and relative abundance of marine and estuarine organisms are greatly influenced by the physico-chemical parameters. Different taxa are affected by wide spectrum of limnological conditions such as pH, nutrient concentrations and salinity. Their number was found to be reduced due to pollution. Variation in pH, salinity temperature regime, solutes, flow, turbidity, dissolved oxygen, substrate composition or pollution level affects fish assemblage. The gain or loss of certain species is a common consequence of the environmental change. The rapid industrialization and the increase in population around the Cochin estuary have resulted in the discharge of a heavy load of the inorganic and organic wastes. Pollution and encroachment are mainly responsible for deterioration of water quality in the water bodies of Kerala.

Key Words: *Pollution, Turbidity, Fish assemblage, Migration, Limnological conditions*

1. Introduction

The Cochin backwater system is a positive tropical estuary which exhibits a unique ecological complex having marine, estuarine and freshwater environments at different zones. It is the largest backwater system of Kerala state, which encompasses a large number of organisms, with its problems and opportunities. It supports rich fishery resources having several species of marine fin fishes and shell fishes and acts as a sink and transformer for the agricultural and municipal wastes discharged into it. The discharge of fresh water from the various rivers and drainage canals cause a dynamic condition which renders the backwater an extremely interesting and

ecologically intriguing environment. The inland extensions of the Cochin backwater system with their very many water enclaves are of utmost important from the fishery point of view and are well known for their role as nursery ground for many of the commercially important species of fishes. The major hydrological variable in the Cochin backwater is salinity (Menon et al., 2000). The salinity gradient in the Cochin back water supports diverse species of flora and fauna according to their tolerance for the saline environments.

The processes regulating the biological productivity in the Cochin backwater is very complex. This estuary is influenced by heavy rain and fresh water influx during monsoon seasons i.e., south west monsoon and north east monsoon. During the peak of south west monsoon, salinity gets very low values all over the regions. High tides from the Arabian Sea contribute a regular flow of salt water, which diminishes considerably towards the head of the Cochin estuary (Madhupratap, 1987). This tropical estuarine environment exhibit multitudinal features (Quasim, 2003) which characterize freshwater and seawater mixing (Menon et al., 2000) and provide breeding ground for marine organisms (Nair et al., 1988; Sarala Devi et al., 1991; Madhu et al., 2007).

Cochin backwater system has been experiencing high levels of anthropogenic pressure during the last five decades (Menon et al., 2000). Reclamation of land for harbour and urban development, intensive exploitation of resources, discharge of untreated or partially treated sewage and industrial effluents resulted in variations in the flushing characteristics and ultimately transforming the system into a eutrophic one. There are environmental problems concerning the shrinking of the estuary and loss of its biodiversity (Gopalan et al., 1980) and in the beginning of the 19th century, the total area of CBW has shrunk from

365km² to 256km² (Gopalan et al., 1983; Balachandran et al., 2005).

Eutrophication due to excess supply of nutrients from industrial and domestic activities influence coastal and estuarine water (Barmawidjaja et al., 1995; Tsujimoto et al., 2006). Reddy et al., (2002) reported that human activities can heavily pollute a lake while studying the eutrophic status of Hussain Sagar Lake. Waste water from industries with high temperature lead marked ill effect on water quality, planktons, and fish fauna of the Lake (Pandey, 1995). The studies on prevailing quality of environment form the basis for understanding impacts of a particular anthropogenic stress (Kulkarni et al., 2011).

Cochin backwater system situated at the tip of the northern Vembanad lake is regarded as a positive tropical estuary located between 9° 14' to 10° 12'N and 76°10' to 76° 36'E with its northern boundary at Azheekode and southern boundary at Thannermukkom bund. The estuary has a length of 80 km and width varies from 500 to 4000m. It has been regarded as the second largest estuarine system in India, fed by six rivers with fresh water discharge of about 291,010 m³ per year (Srinivas et al., 2003). It is permanently connected to Arabian Sea by 450 m wide channel at the bar mouth. There are three seasonal conditions prevailing in the estuary viz., pre monsoon (PRE), monsoon (MON) and post monsoon (POM). During premonsoon

season (February-May), warm climate prevails over the coast, runoff is least and the estuary is predominantly marine in nature. The environment is more or less stable, well mixed and homogenous water mass is present. This estuary is under the profound influence of monsoon (June - September). Hydrobiological studies (Menon et al., 2000) revealed that the high flushing during monsoon completely transforms the estuary into a freshwater habitat. Postmonsoon (October-January) is generally the stabilization period and is characterized by diminished river discharge and tides gradually gain momentum as the estuarine condition change to partially mixed type.

2. Materials and Methods

Seasonal samplings of water, were carried out from the fifteen selected stations (S1 to S15) (figure 1, Table 1) spread across Cochin backwater system. The samples were collected in five sampling campaigns that were scheduled during January 2009, April 2009, August 2009, January 2010 and April 2010, representing three seasons (premonsoon, monsoon and postmonsoon). Water samples (both surface and bottom layers) were collected using Niskin Sampler Water samples for general hydrography and nutrient analysis was subsampled into high density polyethylene bottles, kept on ice bags transported to laboratory and analysed without delay.

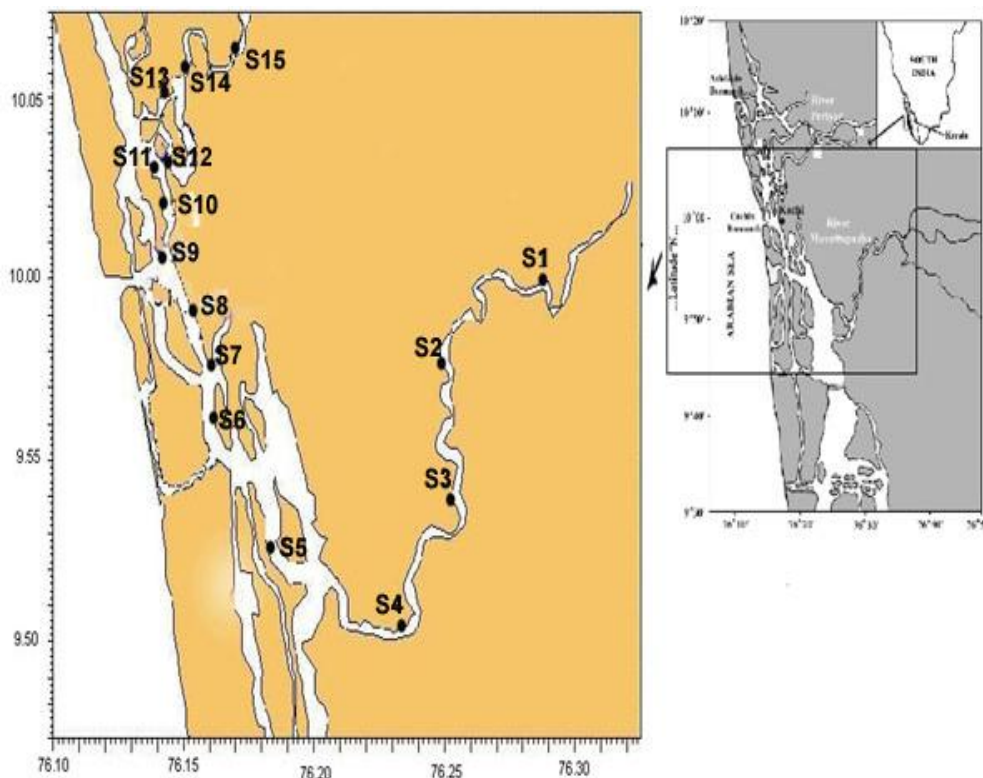


Figure 1 Map showing sampling stations

Table 1 General features of sampling stations

Station Code	Place	Average Depth (m)	Latitude	Longitude	Description
S1	Karippadam	4.3	9° 47.646'N	076° 25.708'E	Thickly populated area with outflow of domestic wastes
S2	Murinjapuzha Enadi	4.4	9° 47.887'N	076° 24.607'E	Disposal of domestic wastes
S3	Murinjapuzha Brahmamangalam	4.9	9° 48.495'N	076° 24.019'E	Disposal of domestic wastes
S4	Murinjapuzha	4.6	9° 49.508'N	076° 23.359'E	Disposal of domestic wastes
S5	Perumbalam	3.2	9° 49.793'N	076° 21.430'E	Disposal of Domestic and fish processing wastes
S6	Aroor-Kumbalam	5.6	9° 53.105'N	076° 18.409'E	Fishing and processing unit operations
S7	Thevara Bridge	2.7	9° 55.070'N	076° 18.253'E	Sewage Outfall
S8	Marine Science Jetty	3.3	9° 57.77'N	076° 16.919'E	Sulphur Jetty input and sewage. Industrial pollution
S9	Bolgatty	2.5	9° 59.213'N	076° 16.084'E	Inland navigation and other tourism operations -waste disposal
S10	Mulavukad	2.2	10° 01.857'N	076° 15.789'E	Disposal of domestic sewages and fish wastes
S11	Chenoor	1.9	10° 03.255'N	076° 16.043'E	Domestic sewages out fall
S12	Cheranellur	2.1	10° 03.999'N	076° 16.924'E	Disposal of domestic sewage and wastes
S13	Eloor	4.4	10° 05.656'N	076° 17.049'E	Industrial Belt
S14	Edayar	2.5	10° 05.502'N	076° 17.744'E	Industrial Belt
S15	FACT-Kalamassery	2.8	10° 04.993'N	076° 17.906'E	Industrial Belt

2.1. General Hydrographic Parameters

Hydrographic parameters such as pH, dissolved oxygen, carbon dioxide, temperature, salinity, alkalinity, hardness, rainfall, depth and transparency were determined. Nutrients like nitrite-N, nitrate-N, ammonia-N, phosphate, silicate, iron were also estimated in the water samples. Rainfall data were obtained from the meteorological Centre, Trivandrum (Govt. of India). Tide data was collected from Cochin Port Trust (Govt. of India). Measurement of transparency of water column was carried out with Secchi disc and extinction coefficient was calculated using the formula (Michael, 1984).

Extinction Coefficient= 1.7/depth in meters

pH measurements of water samples were made using a portable pH meter (Perkin Elmer, accuracy, ± 0.01). Temperature was measured using a precision mercury thermometer graduated from 0-50° C with accuracy of $\pm 0.01^\circ\text{C}$. Immediately after collecting the water sample in a narrow mouthed polyethylene bottle, the thermometer was introduced into the water column

upto 5 cm. Salinity was estimated by Mohr-Knudsen method (Muller, 1999). Modified Winkler method was used for the estimation of dissolved oxygen (Hansen, 1999). Free CO₂ was determined with NaOH reagent and phenolphthalein indicator (Golterman et al., 1978). Alkalinity of the water samples were estimated by the method of Koroleff (Anderson et al., 1999). Five day biochemical oxygen demand test (BOD₅) employed for determination of BOD values of water samples (APHA, 2005). The dissolved oxygen in sample was determined before and after 5 days of incubation.

2.2 Estimation of Nutrients in Water Column.

Nutrients (nitrite, nitrate, phosphate and silicate) were estimated spectrophotometrically using standard methods.

2.2.1 Nitrite

NO₂⁻ was estimated using the standard procedure suggested by Grasshoff et al., (1999) in which the nitrite formed an azodye with sulphanilamide and N-1 naphthyl ethylene diamine dihydrochloride. The spectrophotometric determination was done using UV-Vis

spectrophotometer (Genesys 10 UV-Thermospectronic).

2.2.2 Nitrate

NO_3^- was reduced to NO_2^- using copper coated cadmium granules and determined as nitrite as outlined above (Grasshoff et al., 1999).

2.2.3 Dissolved inorganic phosphate

All methods for the determination of dissolved inorganic phosphate in water samples is based on the reaction of the ions with an acidified molybdate reagent to yield a phosphomolybdate heteropoly acid, which is then reduced to a intense blue coloured compound (Grasshoff et al., 1999). A known volume of sample was treated with mixed reagent and acidified ascorbic acid and the absorbance of the resulting blue complex was measured at 880nm using spectrophotometer.

2.2.4 Silicate

The determination of dissolved silicon compounds in natural water is based on the formation of a yellow silicomolybdic acid when an acid sample is treated with a molybdate solution. This complex was reduced with ascorbic acid and absorbance was measured at 880nm (Grasshoff et al., 1999).

2.2.5 Iron

Water samples were preconcentrated according to Grasshoff et al., (1999); concentration of iron was estimated by Atomic absorption spectrometer (Perkin Elmer 3110).

3. Results

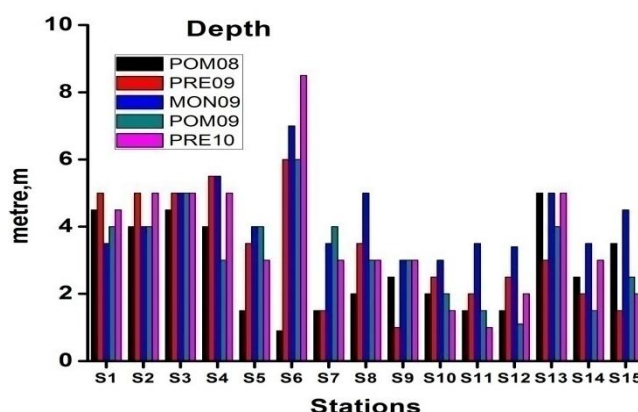
Water samples collected from the selected stations of Cochin backwater were analysed for various physico-chemical parameters. General hydrographic variables, nutrients such as nitrate, nitrite, ammonia, phosphate, silicate and iron were determined in the water samples taken from the CBW. Data regarding rainfall and tides were also collected. Seasonal average concentration of various hydrographic parameters and their spatio-temporal variations were also determined.

3.1 Rainfall

Total rainfall of 367mm was recorded from January 2009 to April 2010. During POM 08, measured rainfall was 18mm and in PRE 09, it was observed to be 154mm. However MON 09 exhibited a rainfall of 180 mm. During POM 09 and in PRE 10, it was 7 and 8mm respectively. Rainfall data were obtained from the meteorological Centre, Trivandrum (Govt. of India).

3.2 Tide

Tide data was collected from Cochin Port Trust (Govt. of India). At the time of collection during POM 08 high tide was observed. During PRE 09, MON 09, POM 09 and PRE 10 low tide was recorded.



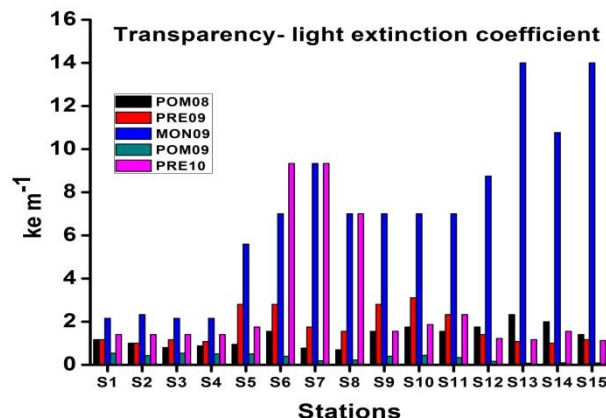


Figure 2 spatial and seasonal variations in depth of stations and transparency

3.3 Depth

Figure 2 provides the variation in depth throughout the investigation period. Out of the 15 sampling stations, during POM 08, an average depth of 2.76 ± 1.36 m was recorded and it varied from 0.9 to 5 m. In PRE 09, average depth was found to be 3.3 ± 1.63 m and it ranged between 1 and 6 m. MON 09 exhibited an average depth of 4.22 ± 1.1 m and it ranged between 3 and 7 m. Measured depth during post MON 09 ranged from 1.1 to 6 m (average: 3.24 ± 1.37 m). However, PRE 10 showed an average depth of 3.63 ± 1.9 m and it varied from 1 to 8.5 m.

3.4 Transparency- light extinction coefficient

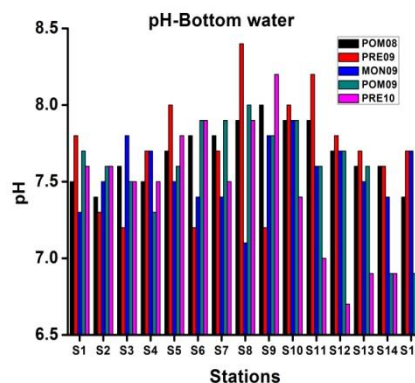
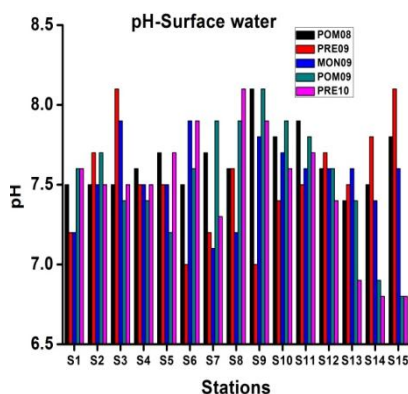
Transparency recorded an average of $1.34 \pm 0.49 \text{ km}^{-1}$ and varied from 0.7 to 2.3 km^{-1} , during POM 08. However in PRE 09, average value was found to be $1.75 \pm 0.79 \text{ km}^{-1}$ and observed values ranged between 1 and 3.11 km^{-1} . MON 09 found to exhibit values varying from 2.15 to 14 km^{-1} with an average of $7.08 \pm 3.91 \text{ km}^{-1}$. The observed variation in transparency during POM 09 was from 0.07 to 0.54 km^{-1} (average: $0.33 \pm 0.17 \text{ km}^{-1}$). In the present investigation, PRE 10 recorded values ranging between 1.12 to 9.33 km^{-1} with an average of $2.92 \pm 2.97 \text{ km}^{-1}$. ANOVA revealed that transparency exhibited only significant seasonal variation ($p < 0.01$).

Spatiotemporal variation in transparency is represented in figure 2.

3.5 pH

Measured values of pH (surface water) during POM 08 ranged between 7.4 and 8.1 with an average of 7.65 ± 0.19 . Meanwhile, in PRE 09, the average value for this variable was found to be 7.52 ± 0.34 and the exhibited variation was from 7 to 8.1. Observed values of pH of the surface water during MON 09 varied from 7.1 to 7.9 (average: 7.54 ± 0.24). During POM 09, average pH recorded was 7.55 ± 0.37 and it varied from 6.8 to 8.1. However during PRE 10, it varied from 6.8 to 8.1 (average: 7.48 ± 0.39).

Average values of pH and its spatiotemporal variation in bottom layers of the water column is furnished in table 3.2 and figure 3.2. During POM 08 (bottom water), values of pH varied from 7.4 to 8 with an average of 7.68 ± 0.20 . In PRE 09, pH ranged between 7.2 and 8.4 (average: 7.7 ± 0.36). Average value of pH was measured to be 7.55 ± 0.21 and it ranged from 7.1 to 7.9 (MON 09). In the case of POM 09, pH of bottom layers varied from 6.9 to 8 (average: 7.59 ± 0.33) and in PRE 10, it varied from 6.7 to 8.2 (average: 7.42 ± 0.44). (figure 3)



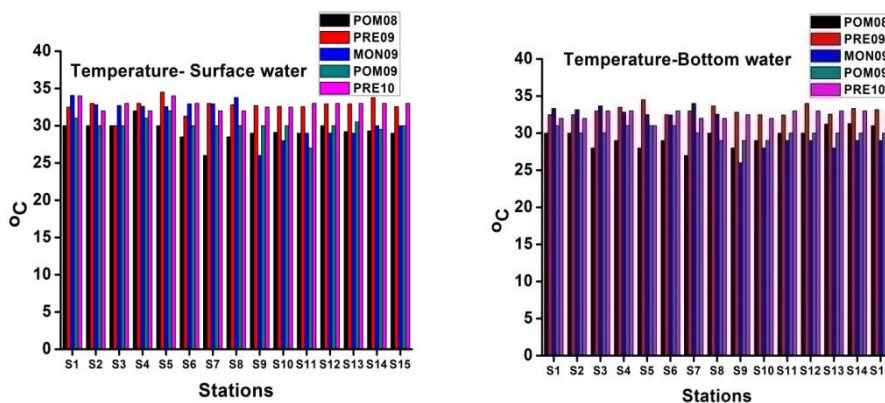


Figure 3 Spatial and seasonal variations in pH and water temperature

3.6 Water - Temperature

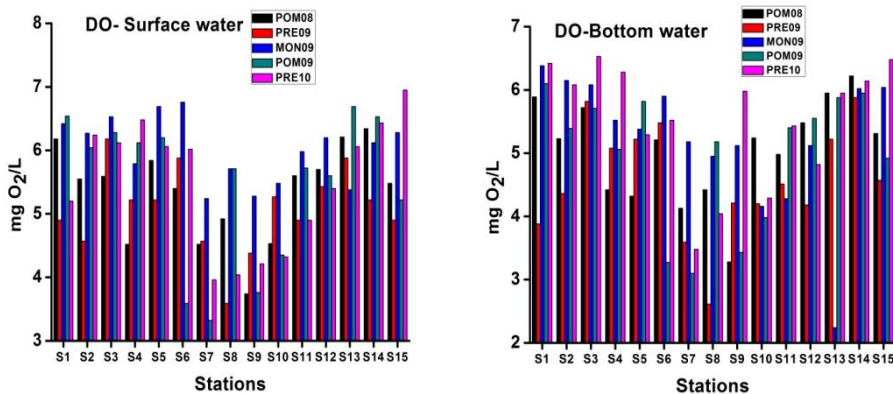
Seasonal variation in temperature of both surface and bottom water is depicted in figure 3. Surface water recorded values for temperature varying from 26 to 32°C (average: $29.30 \pm 1.26^\circ\text{C}$), during POM 08. Meanwhile, PRE 09 exhibited an average of $32.68 \pm 1^\circ\text{C}$ with values ranging between 30 and 34.5°C. The measured temperature of surface water ranged from 26 to 34.06°C with an average value of $31.02 \pm 2.44^\circ\text{C}$ during MON 09. During POM 09 values for surface water temperature varied from 27 to 32°C (average: $30.06 \pm 1.04^\circ\text{C}$) and in PRE 10, it varied from 32 to 34°C (average: $32.8 \pm 0.65^\circ\text{C}$).

During POM 08, average temperature of bottom layers was $29.43 \pm 1.30^\circ\text{C}$ and it varied from 27 to 31.3°C. In PRE 09, temperature of bottom layers ranged between 32.44 and 34.5°C with an average of $33.06 \pm 0.62^\circ\text{C}$. However the observed values of temperature in bottom water, during MON 09, ranged from 26 to 34°C (average: $30.83 \pm 2.60^\circ\text{C}$). During POM 09, temperature of bottom water varied from 29 to 31°C with an average of $30.06 \pm 0.70^\circ\text{C}$ and in PRE 10, it varied from 31 to 33°C (average: $32.5 \pm 0.62^\circ\text{C}$).

3.7 Dissolved oxygen (DO)

During POM 08, dissolved oxygen (surface water) varied from 3.74 to 6.34mg/L with an average of $5.3 \pm 0.7\text{mg/L}$. In PRE 09, DO range between 3.59 and 6.18mg/L (average: $5.07 \pm 0.66\text{mg/L}$). It recorded an average content of $6 \pm 0.5\text{mg/L}$ with a variation from 5.24 to 6.76mg/L during MON 09. During POM 09, it ranged from 3.32 to 6.69mg/L and recorded an average of $5.4 \pm 1.1\text{mg/L}$. In the present study, PRE 10 an average concentration of $5.49 \pm 0.99\text{mg/L}$ and the observed DO content found to range between 3.96 to 6.95mg/L. The variation in concentration of DO in surface and bottom water is depicted in figure 4.

In bottom water of the study area during POM 08, DO varied from 3.28 to 6.22mg/L, with an average of $5.05 \pm 0.80\text{mg/L}$. In PRE 09, DO showed an average content of $4.58 \pm 0.88\text{mg/L}$ and ranged from 2.61 to 5.88 mg/L. During MON 09, the value varied from 2.24 to 6.38mg/L (average: $5.23 \pm 1.06\text{mg/L}$). However, recorded DO content during POM09 ranged between 3.1 and 6.1mg/L with an average of $4.98 \pm 1.02\text{mg/L}$. The average DO content estimated during PRE 10 was observed to be $5.51 \pm 0.95\text{mg/L}$, and its content during this period ranged between 3.48 and 6.53 mg/L.



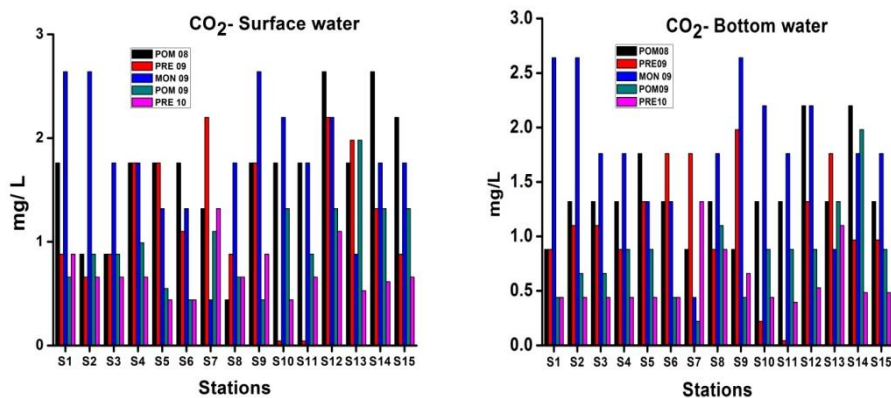


Figure 4 Spatial and seasonal variations in DO and CO₂ in water from the study area

3.8 Carbon Dioxide

Content of free carbon dioxide (surface water) during POM 08 varied from 0.44 to 2.64mg/L with an average of 1.67 ± 0.60 mg/L. In PRE 09, CO₂ exhibited an average of 1.2 ± 0.70 mg/L and ranged between 0.44 and 2.2 mg/L (figure 4). Concentration of CO₂ recorded an average of 1.7 ± 0.6 mg/L and ranged between 0.4 to 3.0mg/L, during MON 09. However, during POM 09, it ranged from 0.44 to 1.98mg/L (average: 0.98 ± 0.04 mg/L). Present study revealed that during PRE 10, the average CO₂ content was found to be 0.7 ± 0.2 mg/L and exhibited variation was from 0.44 to 1.32mg/L.

During POM 08, CO₂ (bottom water) varied from 0.88 to 2.2mg/L (average: 1.0 ± 0.40 mg/L). In PRE 09, CO₂ recorded an average content of 1.0 ± 0.5 mg/L and it ranged from 0.04 to 2.0mg/L. During MON 09, it found to vary from 0.4 to 3.0 mg/L with an average of 2.0 ± 0.6 mg/L. During POM 09, the average concentration was observed to be 0.8 ± 0.4 mg/L and exhibited a variation from 0.22 to 1.98mg/L. The recorded content of CO₂ during PRE 10 ranged between 0.4 to 1.3mg/L (average: 0.06 ± 0.2 mg/L) (figure 4).

3.9 Biochemical oxygen demand (BOD)

Surface water of the study area during POM 08 recorded BOD values varying from 0.22 to 6.2mg/L (figure 5) with an average of 2.4 ± 1.73 mg/L. Meanwhile, PRE 09 recorded values ranging between 0.62 and 5.41mg/L (average: 3.64 ± 1.56 mg/L). BOD recorded an average value of 2.02 ± 1.54 mg/L during MON 09 and it ranged between 0.29 and 4.98mg/L. Average value BOD was estimated to be 2.54 ± 1.85 mg/L and it ranged from 0.16 to 6.24mg/L during POM 09. During PRE 10, values of BOD ranged between 0.64 to

5.76mg/L with an average of 4.11 ± 1.73 mg/L.(figure 5)

During POM 08, BOD values in bottom water varied from 0.14 to 5.96mg/L with an average value of 2.24 ± 2.02 mg/L (table 3.2). In PRE 09, it recorded a variation ranged between 0.5 to 5.98mg/L (average: 3.53 ± 1.58 mg/L). Meanwhile, MON 09 recorded an average BOD value of 2.28 ± 1.53 mg/L and exhibited variation from 0.18 to 5.1mg/L. The estimated average during POM 09 was 2.3 ± 2.3 mg/L, and the observed values ranged from 0.16 to 6.88g/L. PRE 10, value ranged between 0.64 to 6.72mg/L (average: 4.4 ± 1.8 mg/L). (ANOVA) displayed highly significant seasonal and spatial variation ($p < 0.01$) for both surface and bottom layers.

3.10 Salinity

During POM 08, salinity in surface water varied from 3.47 to 32 psu with an average of 17.11 ± 9.37 psu. In PRE 09, exhibited an average value of 10.53 ± 8.93 psu and ranged from 1.57 to 28.89 psu. Estimated salinity during MON 09 varied from 3.47 to 17.52 psu with an average of 11.12 ± 10.10 psu. However during POM 09, it ranged between 1.28 and 29.93 psu (average: 11.12 ± 10.08 psu). While in PRE 10, it ranged between 0.71 to 29.46 psu with an average of 8.82 ± 8.11 psu.

During POM 08, salinity in bottom water varied from 3.47 to 33.72 psu with an average value of 19.01 ± 9.83 psu (table 3.2). The observed average value for salinity during PRE 09, ranged from 1.57 to 29.52psu (average: 12.09 ± 8.5 psu). Average salinity estimated during MON 09 was found to be 9.12 ± 6.67 psu and revealed a variation from 3.47 to 24.32psu. During POM 09, salinity ranged from 1.28 to 31.38psu and it displayed an average of 11.33 ± 9.43 psu. But during PRE 10, it ranged from 0.59 to 33.5 psu and recorded an average of 11.52 ± 11.22 psu.

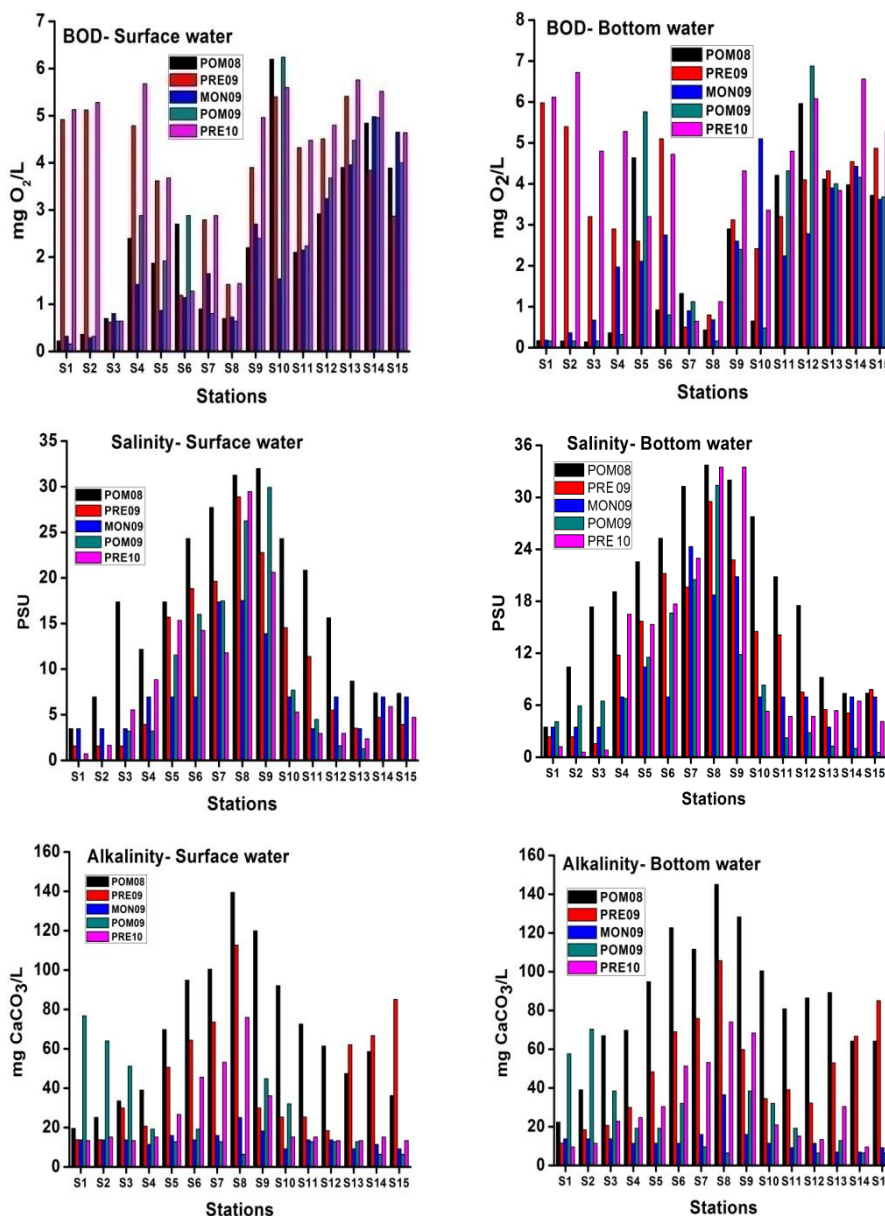


Figure 5 Spatial and seasonal variation in BOD, salinity and alkalinity in water from the study area

3.11 Alkalinity

During POM 08 alkalinity in surface water varied from 19.53 to 140mgCaCO₃/L (average: 67.33±35.82 mgCaCO₃/L). In PRE 09, alkalinity ranged between 13.8 to 112.7 mgCaCO₃/L with an average of 16.15±30.04 mgCaCO₃/L. The recorded average for this variable 13.83±4.08 mgCaCO₃/L during MON 09 ranged between 9.12 to 25.08 mgCaCO₃/L. It was observed that during POM 09 value ranged from 6.4 to 76.8mg/L and the recorded average was 26.02±22.62 mgCaCO₃/L. Meanwhile, PRE 10 represented the minimum of 13.3 and maximum of 76mgCaCO₃/L (average: 25.3±19.10 mgCaCO₃/L).

During POM 08, an average alkalinity value of 85.74±33.22 mgCaCO₃/L (bottom water) and observed variation was from 22.32 to 145.08 mgCaCO₃/L. Meanwhile PRE 09 showed an average

of 49.98±26.96 mgCaCO₃/L ranged between 11.5 and 105.8 mgCaCO₃/L. During MON 09, alkalinity ranged between 6.84 to 36.48 mgCaCO₃/L (average: 13.22±7.01mgCaCO₃/L). Alkalinity with an average of 24.96±19.73 mgCaCO₃/L during POM 09 and it ranged from 6.4 to 70.4 mgCaCO₃/L. Estimated value during PRE 10, ranged between 9.5 and 74.1 mgCaCO₃/L and displayed an average of 29.89±21.60 mgCaCO₃/L. Analysis of variance (ANOVA) revealed only highly significant seasonal variation ($p < 0.01$) for surface water. However, bottom water exhibited both seasonal and spatial variation ($p < 0.01$). During MON 09, the values were lower compared to other seasons in both surface and bottom water of the study area (figure 5).

3.3 Nutrients in Water Column

3.3.1 Ammonia-N

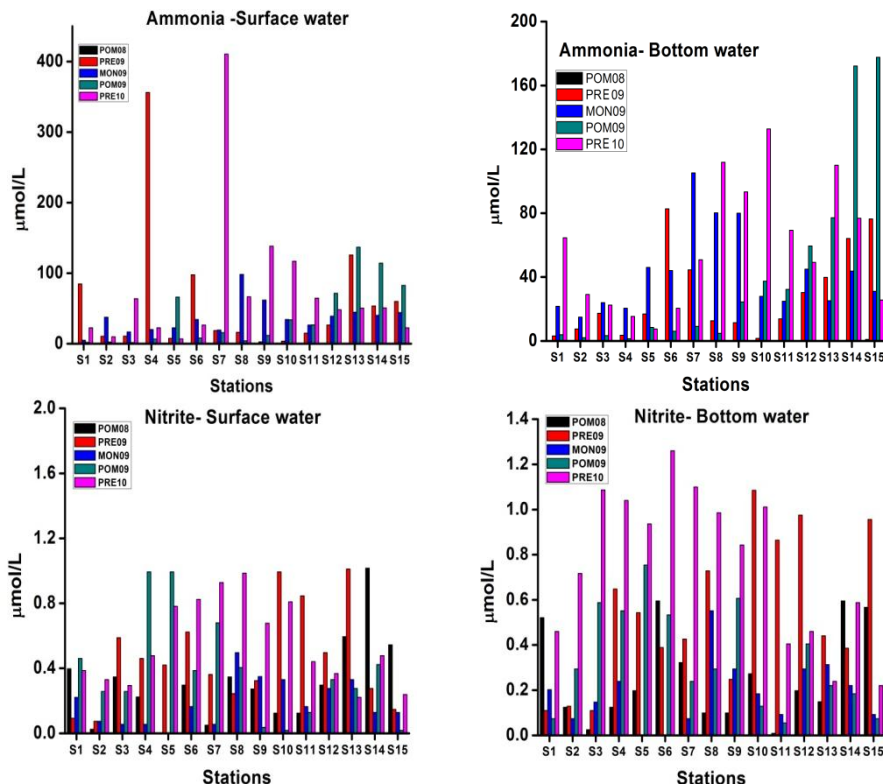
In the surface water samples collected during POM 08, ammonia content varying from 0.07 to 0.38 $\mu\text{mol/L}$ with an average of $0.16 \pm 0.09 \mu\text{mol/L}$. Concentration of ammonia ranged between 2.6 and 356.1 $\mu\text{mol/L}$ and the estimated average concentration was found to be $59.24 \pm 90.62 \mu\text{mol/L}$, in the PRE 09. The variation was 4.72 to 98.09 $\mu\text{mol/L}$ during MON 09 (average: $36.21 \pm 22.14 \mu\text{mol/L}$). Average ammonia content (POM 09) was found to be $38.89 \pm 44.49 \mu\text{mol/L}$ and the observed range for this variable was from 1.57 to 136.70 $\mu\text{mol/L}$. During PRE 10 value ranged between 6.69 to 410.50 $\mu\text{mol/L}$ (average: $74.69 \pm 100 \mu\text{mol/L}$).

During POM 08, concentration of ammonia in bottom water varied from 0.02 to 0.96 $\mu\text{mol/L}$ and recorded an average of $0.19 \pm 0.22 \mu\text{mol/L}$. In PRE 09, ammonia ranged between 1.57 and 82.73 $\mu\text{mol/L}$ (average: $28.38 \pm 27.19 \mu\text{mol/L}$). During MON 09, concentration of ammonia recorded an average of 42.29 ± 26.38 and it varied from 14.97 to 105.2 $\mu\text{mol/L}$. During POM 09, its concentration ranged from 1.34 to 177.70 $\mu\text{mol/L}$ with an average of $41.31 \pm 58.80 \mu\text{mol/L}$. While during PRE 10, concentration ranged between 7.48 and 132.80 $\mu\text{mol/L}$ (average: $58.62 \pm 39.66 \mu\text{mol/L}$).

During POM 08 nitrate in the surface water varied from 3 to 47.3 $\mu\text{mol/L}$ and recorded average of $13.58 \pm 12.78 \mu\text{mol/L}$. In PRE 09, nitrate ranged between 2.3 to 27.2 $\mu\text{mol/L}$ with an average of $10.05 \pm 6.87 \mu\text{mol/L}$. Average concentration of nitrate in surface water of the study area, during MON 09 was found to be $30.63 \pm 70.89 \mu\text{mol/L}$ and it ranged from 6.20 to 290.30 $\mu\text{mol/L}$. During POM 09, value ranged from 1.2 to 15.4 $\mu\text{mol/L}$ and displayed an average content of $8 \pm 4.88 \mu\text{mol/L}$. While in PRE 10, concentration of nitrate varied from 0.93 to 30.50 $\mu\text{mol/L}$ with an average of $9.56 \pm 8.54 \mu\text{mol/L}$.

The bottom water of the study area during POM 08 exhibited a variation nitrate concentration from 0.53 to 177.4 $\mu\text{mol/L}$ (average: $20.96 \pm 44.2 \mu\text{mol/L}$). In PRE 09, nitrate ranged between 0.88 and 17.4 $\mu\text{mol/L}$ and recorded an average of $7.81 \pm 4.96 \mu\text{mol/L}$. While during MON 09, its content ranged from 7.5 to 41.89 $\mu\text{mol/L}$ and the estimated average was found to be $21.04 \pm 12.55 \mu\text{mol/L}$. During POM 09, the nitrate content ranged from 2.3 to 15.6 $\mu\text{mol/L}$ with an average of $7.96 \pm 3.88 \mu\text{mol/L}$. Meanwhile concentration of this variable during PRE 10, ranged between 0.79 and 25.6 $\mu\text{mol/L}$ and displayed an average of $10.59 \pm 8.5 \mu\text{mol/L}$. Statistical analysis of variance displayed only significant spatial variation.

3.3.2 Nitrate-N



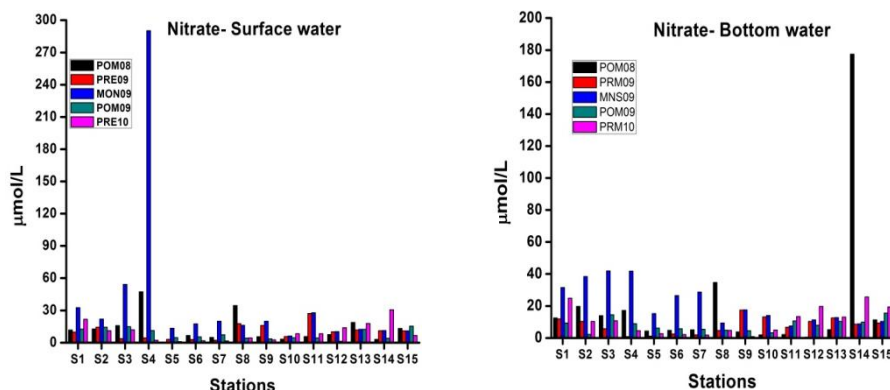


Figure 6 Spatial and seasonal variation in ammonia, nitrite and nitrate in water from the study area

3.3.3 Nitrite

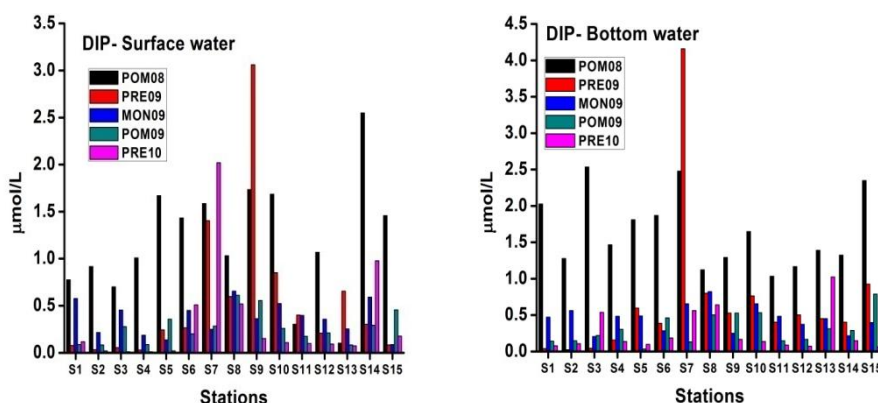
During POM 08 nitrite in the surface water varied from 0.03 to 1.02 $\mu\text{mol/L}$ and the estimated average was found to be $0.33 \pm 0.25 \mu\text{mol/L}$. In PRE 09, nitrite ranged between 0.07 and 1.01 $\mu\text{mol/L}$ with an average content of $0.46 \pm 0.30 \mu\text{mol/L}$. While during MON 09, the recorded average concentration of nitrite was $0.20 \pm 0.13 \mu\text{mol/L}$ and it varied from 0.05 to 0.49 $\mu\text{mol/L}$. However, during POM 09, the concentration of nitrite ranged from 0.02 to 0.99 $\mu\text{mol/L}$ (average: $0.37 \pm 0.30 \mu\text{mol/L}$). In the present investigation, concentration of nitrite during PRE 10 ranged between 0.221 and 0.986 $\mu\text{mol/L}$ and recorded an average of $0.54 \pm 0.25 \mu\text{mol/L}$.

While in bottom layers, the concentration of nitrite during POM 08 exhibited a variation from 0.01 to 0.59 $\mu\text{mol/L}$ with an average of $0.26 \pm 0.21 \mu\text{mol/L}$. PRE 09 exhibited concentration of nitrite varying from 0.11 to 1.09 $\mu\text{mol/L}$ with an average of $0.53 \pm 0.32 \mu\text{mol/L}$. The estimated average concentration for this variable was found to be $0.53 \pm 0.32 \mu\text{mol/L}$ (POM 09) and it nitrite ranged from 0.11 to 1.09 $\mu\text{mol/L}$. However, during MON 09 its content ranged between 0.07 and 0.55 $\mu\text{mol/L}$ and revealed an average of $0.21 \pm 0.13 \mu\text{mol/L}$. Concentration of Nitrite during PRE 10 displayed an average of $0.75 \pm 0.33 \mu\text{mol/L}$ and it ranged between 0.22 and 1.26 $\mu\text{mol/L}$. (figure 6)

3.3.4 Dissolved Inorganic Phosphate (DIP)

Spatiotemporal variation in DIP is represented in figure 8. During POM 08 phosphate in the surface water ranged between 0.10 and 2.55 $\mu\text{mol/L}$ (Avg $1.20 \pm 0.62 \mu\text{mol/L}$). During POM 09, it varied from 0.03 to 3.06 $\mu\text{mol/L}$ and exhibited an average concentration of $0.55 \pm 0.79 \mu\text{mol/L}$. The content of dissolved inorganic phosphate during MON 09 recorded an average of $0.36 \pm 0.17 \mu\text{mol/L}$ and it ranged between 0.08 to 0.65 $\mu\text{mol/L}$. Meanwhile, during POM 09, its content varied from 0.03 to 3.06 $\mu\text{mol/L}$ and the estimated average was found to be $0.55 \pm 0.79 \mu\text{mol/L}$. Average concentration of dissolved inorganic P was found to be $0.32 \pm 0.53 \mu\text{mol/L}$ and it ranged between 0.01 and 2.02 $\mu\text{mol/L}$ (PRE 10).

Content of inorganic phosphate during POM 08 (bottom water) of the study area varied from 1.03 to 2.53 $\mu\text{mol/L}$ and recorded average of $1.65 \pm 0.50 \mu\text{mol/L}$. In PRE 09, phosphate ranged between 0.02 and 4.15 $\mu\text{mol/L}$ and exhibited an average concentration of $0.67 \pm 1.0 \mu\text{mol/L}$. Average concentration of phosphate during MON 09 was observed to be $0.45 \pm 0.17 \mu\text{mol/L}$ and this variable ranged from 0.20 to 0.82 $\mu\text{mol/L}$. While, in POM 09, the observed variation in concentration was from 0.03 to 0.78 $\mu\text{mol/L}$ and the estimated average was found to be $0.31 \pm 0.2 \mu\text{mol/L}$. Concentration of DIP during PRE 10 ranged between 0.06 and 1.02 $\mu\text{mol/L}$ (average: $0.26 \pm 0.28 \mu\text{mol/L}$) (Figure 7).



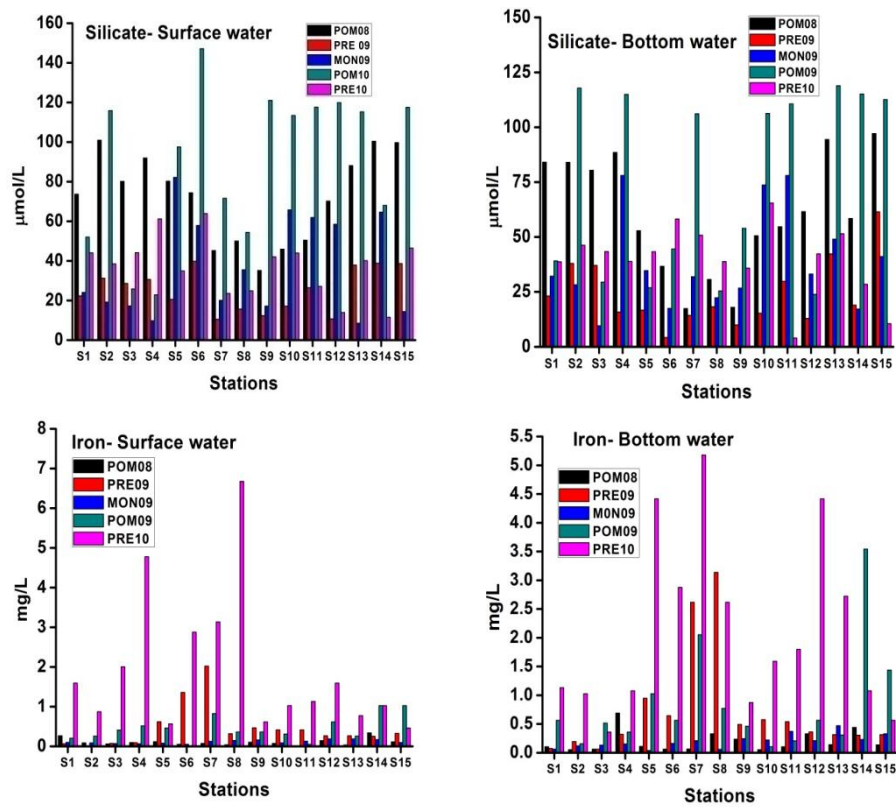


Figure 7 Spatial and seasonal variation in DIP, silicate and iron in water from the study area

3.3.5 Silicate

Concentration of silicate (surface water) during POM 08 ranged from 35.2 to 101 $\mu\text{mol/L}$ and recorded an average of $72.46 \pm 22.23 \mu\text{mol/L}$. It ranged between 10.54 and 39.78 $\mu\text{mol/L}$, with an average of $25.43 \pm 10.67 \mu\text{mol/L}$ (PRE 09). Meanwhile, during MON 09, the silicate content ranged from 8.52 to 82.16 $\mu\text{mol/L}$ and recorded an average of $37.1 \pm 25.03 \mu\text{mol/L}$. Average concentration of silicate during POM 09 was found to be $90.70 \pm 38.48 \mu\text{mol/L}$ and estimated concentration varied from 22.83 to 147.2 $\mu\text{mol/L}$. During PRE 10, its content ranged between 11.49 to 63.91 $\mu\text{mol/L}$ (average: $37.37 \pm 15.11 \mu\text{mol/L}$).

During POM 08, silicate in bottom water varied from 17.45 to 97.08 $\mu\text{mol/L}$ and the estimated average was found to be $60.64 \pm 26.84 \mu\text{mol/L}$ (Figure 7). In POM 09, the concentration ranged from 4.22 to 61.45 $\mu\text{mol/L}$ and recorded an average of $23.88 \pm 15.11 \mu\text{mol/L}$. In the present study, during MON 09 it ranged between 9.52 and 78 $\mu\text{mol/L}$ (average: $38.22 \pm 22.10 \mu\text{mol/L}$). POM 09 recorded a minimum of 23.87 and maximum of 118.9 $\mu\text{mol/L}$ and exhibited an average of $6.38 \pm 41.12 \mu\text{mol/L}$. Silicate concentration in bottom water during PRE 10 varied from 3.95 to 65.52 $\mu\text{mol/L}$ and displayed an average of $39.76 \pm 16.08 \mu\text{mol/L}$.

3.3.6 Iron

Spatiotemporal variation in concentration of iron in surface and bottom layers is furnished in figure 3.6. During POM 08, iron in the surface water varied from 0.01 to 0.34 mg/L and recorded an average $0.10 \pm 0.08 \text{mg/L}$. In PRE 09, it ranged between 0.005 and 2.02 mg/L with an average of $0.46 \pm 0.53 \text{mg/L}$. The average concentration of dissolved Iron was $0.11 \pm 0.04 \text{mg/L}$ and it varied from 0.052 to 0.188 mg/L, during MON 09. Exhibited variation in dissolved iron content during POM 09 was from not detected to 1.03 mg/L and average concentration was found to be $0.44 \pm 0.31 \text{mg/L}$. During PRE 10, it ranged between 0.46 and 6.67 mg/L (average: $1.94 \pm 1.776 \text{mg/L}$).

It was observed that during POM 08, iron in bottom water varied from 0.05 to 0.69 mg/L and exhibited an average of $0.19 \pm 0.18 \text{mg/L}$ (3.2). The observed average Fe content during PRE 09 was $0.72 \pm 0.90 \text{mg/L}$ and it ranged between 0.063 and 3.136 mg/L. During MON 09, its concentration varied from 0.04 to 0.47 mg/L (average: $0.20 \pm 0.12 \text{mg/L}$). Meanwhile, during POM 09 its content ranged from 0.10 to 3.54 mg/L with an average of $0.84 \pm 0.90 \text{mg/L}$. During PRE 10, its content was found to fluctuate between 0.35 and 5.18 mg/L and recorded an average of $2.11 \pm 1.53 \text{mg/L}$.

4. Discussion

Rainfall is the most important cyclic phenomenon in tropical countries as it brings important changes in the hydrographical

characteristics of the marine and estuarine environments. During the present study, the maximum rainfall was recorded during south west monsoon. In the present study, the peak values of rainfall were recorded during MON 09. The rainfall in India is largely influenced by two monsoons viz., southwest monsoon on the west coast, northern and northeastern India and by the northeast monsoon on the southeast coast (Perumal, 1993).

Temperature of surface water is always influenced by the intensity of incident solar radiation, evaporation, freshwater influx and cooling and mix up with ebb and flow from adjoining neritic water. The surface and bottom water temperature (average) during post monsoon was lower because of strong land sea breeze and underwater currents and the recorded high value during premonsoon could be attributed to higher insolation rate of solar radiation (Karuppasamy and Perumal, 2000; Senthilkumar et al., 2002; Santhanam and Perumal, 2003). In the present investigation, there was no spatial variation ($p > 0.05$) observed in temperature which could be due to the lack of viable intensity of prevailing streams and the resulting mixing of water (Reddi et al., 1993). Statistical analysis (ANOVA) showed that there is no spatial variation and therefore be concluded that stations are almost similar temperature, but with high seasonal variation ($p < 0.01$). Present study recorded the minimum temperature at S9 (MON 09) and maximum at S5 (PRE 09).

The tidal mixing and estuarine circulation are crucial factors influencing the hydrographic status of an estuary which in turn affect the nutrient distribution and productivity. Cochin backwater system is characterized by an ox-bow shape, running parallel to Arabian Sea (Soman, 1997). Due to its peculiar topography, the circulation patterns in the northern and southern arms of the CBW are found to be different (Ramamirtham and Muthusamy, 1986). The higher freshwater flow during summer monsoon suppresses the tidal characteristics and increases stratification in the lower estuary (Qasim and Gopinathan, 1969). Tides at Cochin estuarine system are of a mixed semi-diurnal type, with the maximum spring tide range of about 1m (Srinivas, 1999), resulting in incomplete flushing. Hydrobiological studies of the estuary (Menon et al., 2000) showed that the high flushing during monsoon completely transforms the estuary into a freshwater habitat.

Wide fluctuations in the values of transparency might be due to discharge of water due to floating sediments carried by the river from catchment areas. Dredging operations to maintain the average depth of ship channel, Cochin harbour area, Cochin Shipyard and Vallarpadom Container Terminal region, generates huge loads of suspended sediments which affect the transparency of water column. It is evident that heavy rainfall and intense

cloud cover prevailing in the monsoon season reduces solar insolation and the high input of suspended sediments makes the estuary more turbid (Renjith et al., 2012). However, during the post-monsoon period, the excess nutrients carried to the estuarine system through the land runoff, increased solar radiation and reduction in turbidity result in the development of an ideal environment for high primary production. In the present investigation, the estimated light attenuation coefficient was higher during MON 09, a similar observation reported by Madhu et al., 2009 and thereby the light limitation significantly reduces the primary production during this particular season. Generally, higher attenuation values are expected in the monsoon months especially during flood conditions due to likely increase in turbidity of the water and low intensity of solar radiation due to the intense mixing of water having heavy loads of suspended particulate matter (Sarala Devi, 1989). Low values of extinction coefficients were recorded during premonsoon months, which indicated a higher transparency.

Significant spatial and temporal variability of physico-chemical characteristics and productivity patterns are among the important characteristics of estuaries (Renjith et al., 2012). Physico-chemical parameters like nutrient concentrations, algal chlorophyll, water transparency (Carlson, 1977; Kratzer and Brezonik, 1981) and primary production measurements (Nixon, 1995) have often been employed to assess trophic status of water.

In the present investigation, the values of pH in both surface and bottom water remained slightly alkaline at all the stations. Recorded pH during POM 10 was maximum at S9 (surface water), but in maximum was recorded at S8 (bottom water) during PRE 09. Generally, fluctuations in pH values during different seasons of the year is attributed to factors like removal of CO₂ by photosynthesis through bicarbonate degradation, dilution of seawater by freshwater influx, low primary productivity, reduction of salinity and temperature and decomposition of organic materials (Karuppasamy and Perumal, 2000; Rajasegar, 2003). Higher values for pH were recorded during summer seasons, which might be due to the influence of seawater ingress, increased photosynthetic activity (Subramanian and Mahadevan, 1999). The statistical analysis also revealed that salinity showed highly significant negative correlation with rainfall. In the present study, pH (bottom layers) showed highly significant positive correlation with salinity and alkalinity which might be attributed to the fact that rise in pH values associated with increasing salinity and alkalinity, is a general phenomenon observed in aquatic systems.

The maximum DO content was recorded at FACT- Kalamassery (S15) (surface) and at Murinjapuzha –Brahmamangalam(S3) (bottom) during PRE 10. Statistical analysis (ANOVA) showed that there is much seasonal and spatial

variation in DO (both surface and bottom layers). It is well known that the temperature and salinity affect the dissolution of oxygen (Vijayakumar et al., 2000). In the present investigation, higher content for dissolved oxygen was recorded during monsoon, which could be due to the cumulative effect of higher wind velocity joined with heavy rainfall and the resultant freshwater mixing (Das et al., 1997). Mitra et al., (1990) mainly attributed seasonal variation of DO to freshwater flow and terrigenous impact of sediments. Further, significant inverse relationship between rainfall and nutrients indicated that freshwater flow constituted the main source of the nutrients in the estuary. In surface water, the negative correlation of DO with salinity implied the general fact that solubility of oxygen decreases with increase in salinity.

Phytoplankton photosynthesis drives many biogeochemical and ecological processes in lakes, estuaries, and the ocean. Dynamic changes in pH, trace metal speciation, and concentrations of dissolved gases (oxygen and carbon dioxide), inorganic nutrients (nitrate, phosphate, silicate), and organic compounds (amino acids, organosulfur compounds) are all closely associated with fluctuations in phytoplankton photosynthesis. Trophic linkages also exist, between the phytoplankton as primary producers and populations of consumer organisms including bacteria, zooplankton, benthic invertebrates, and fish.

Biochemical oxygen demand depends on temperature, extent of biochemical activities, concentration of organic matter and such other related factors. Maximum value of BOD was observed in pre monsoon period due to the restricted flow of oxygenated water from upper reaches of the contributing river (Renjith et al., 2012). The higher biological production coupled with sinking of organic matter also leads to a high oxygen demand in the water column (Martin et al., 2010). Rapid industrialisation and urbanization in the around Cochin area has resulted in a daily discharge of about 104 million litres of untreated effluents and 260 m³ of raw sewage into the backwater system (Qasim 2003; Balachandran et al., 2005). Waste disposal from aquaculture fields and agricultural fields have worsened the organic pollution in this unique aquatic system. The combined effects of all these factors might be contributed to the increased BOD levels in the study area.

Both surface and bottom water exhibited spatial and seasonal variation ($p < 0.01$) for salinity. In the present investigation, no vertical stratification was observed and fresh water conditions were prevalent during the monsoon season. However, stratification was observed during the post-monsoon season. Higher values for salinity noticed during post monsoon season could be due to increased rate of evaporation and the neritic water dominance. The salinity acts as a limiting factor in the distribution of

living organisms, and its variation caused by dilution and evaporation is most likely to influence the fauna in the intertidal zone. Generally, changes in the salinity in the brackish water habitats like backwater might be due to the influx of freshwater from land run off, caused by monsoon or by tidal variations. In the study area, POM 08 recorded higher values which could be attributed due to the higher tidal inflow of saline water. During the monsoon season, the rainfall and the freshwater inflow from the land in turn moderately reduced the salinity (Govindasamy et al., 2000; Gowda et al., 2001; Rajasegar, 2003; Qasim, 2003). It was observed that during the present investigation, salinity displayed highly significant negative correlation with DO indicating the fact that higher salinity inhibits the dissolution of atmospheric oxygen.

Analysis of variance was carried out to compare the free CO₂ in the surface and bottom water which revealed no significant difference among the stations. In the present investigation concentration of CO₂ found to exhibit highly significant seasonal variation ($p < 0.01$). Estuaries have been regarded as a significant source of CO₂ to the atmosphere (Frankignoulle et al., 1998). This CO₂ is produced in high concentrations in estuarine regions which were known to be heterotrophic systems, where organic carbon transported by rivers is partly mineralized (Gattuso et al., 1998).

Nutrient levels are important determinants of biodiversity, influencing the processes of competition and community structure in the water bodies. In the pelagic water, concentration levels of inorganic nutrients such as nitrate, phosphate and silicate in the water dictate population growth of planktonic primary producers. Rates or pathways through which exogenous nutrients are converted into algal biomass is different among estuaries (Cloern, 2001). Eutrophication caused by excess supply of nutrients from industrial and domestic activities can influence coastal and estuarine water (Barmawidjaja et al., 1995; Tsujimoto et al., 2006). Increased input of nutrient to the CBW is not only from the rivers but also contributed by increased industrial and domestic activities (Jyothibabu et al., 2006). Monsoon rain, after the dry summer period (January to May) washes the adjacent land area and drain nutrient enriched water to CBW, making the system highly productive (Qasim, 2003; Madhu et al., 2007).

Nutrients are generally considered to be the limiting factors for phytoplankton productivity. The nutrient content of estuaries is determined by their concentration in the riverine and coastal water sources. Generally nitrate, nitrite, phosphate and silicate are regarded as essential nutrients for plankton growth which affects the survival and population fluctuation of other fauna and flora in the food chain (Pramodbabu, 2007). The changes and seasonal cycles of these nutrients control most of the

biological activities in estuarine systems. The nitrogen as nitrate and phosphorus as phosphate greatly augment the primary productivity and both are essential for the survival of primary producers, yet they subsist in very small concentration in the surrounding medium. Very low concentration of silicon present in the water can limit phytoplankton production due to the suppression of metabolic activities of the cell. Silicon represents a vital nutrient for the skeletal growth of diatoms (Pramodbabu, 2007).

In the present investigation, average values of ammonia was found to be higher during premonsoon season (figure 7) and this may be partly 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, 1994; Rajasegar, 1998). Some stations exhibited higher values that may be due to industrial effluents and terrestrial input. Ammonia displayed a non-uniform distribution throughout the entire study period which indicated an exogenic input in the estuary (Renjith et al., 2011; Renjith et al., 2012).

The recorded maximum for nitrate content (37.63 $\mu\text{mol/L}$) during monsoon season (figure 7) could be mainly due to the organic materials received from the catchment area during ebb tide and similar results were also recorded by Das et al., 1997. Besides, the increased nitrate level was due to fresh water inflow, organic decomposition and terrestrial run-off during the monsoon season and previous literature by Karuppasamy and Perumal, (2000) supports these facts. Another possible way of nitrates entry is through oxidation of ammonia form of nitrogen to nitrite formation (Rajasegar, 2003). The minimum concentration of (8 $\mu\text{mol/L}$) was recorded during post monsoon period may be due to its utilization by phytoplankton as evidenced by high photosynthetic activity apart from the neritic water dominance, which contained negligible amount of nitrate (Gouda and Panigrahy, 1995; Das et al., 1997; Govindasamy et al., 2000). In the present investigation, the increased in nitrate content observed during the monsoon season, higher content in the low saline stations and the significant negative correlation with salinity, indicated the riverine input (Renjith et al., 2012). Moreover, nitrate in water column showed highly significant positive correlation with DO which inferred the fact that oxygenated condition favoured the formation of nitrate.

In the present investigation the nitrite content was lower during monsoon season (figure 7). Nitrite exhibited its maximum at S14 (POM 08) in surface and S6 (PRE 10) in bottom water. Average nitrite content in surface and bottom water was also found to be higher during the pre monsoon and which could be attributed due to the variation in phytoplankton, excretion and oxidation of ammonia

and reduction of nitrite (Kannan and Kannan, 1996). The lower contents of nitrite during the premonsoon season were due to less freshwater input, higher salinity, pH and also uptake by phytoplankton. The similar situation has already been reported (Edwards and Ayyakannu, 1991; Mathevan, 1994). Highly significant seasonal variation (p value < 0.01) was recorded for this parameter in the case both surface and bottom water.

Both surface and bottom water exhibited lower content for phosphorous during PRE 10 (Figure 7), which could be attributed to the limited flow of freshwater, high salinity and utilization of phosphate by phytoplankton (Senthilkumar, et al., 2002; Rajasegar, 2003). PRE 09 exhibited higher phosphate concentration due to high rainfall and freshwater inflow compared to PRE 10. 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 (Das et al., 1997; Senthil Kumar et al., 2002). Analysis of variance applied to test the significance of difference between stations showed that phosphate concentration differ spatially in surface water ($p < 0.05$) compared to bottom water ($p > 0.05$). The variation may be due to the processes like adsorption and desorption of phosphates and buffering action of sediment under varying environmental conditions (Rajasegar, 2003). The higher phosphate content in the water column could be attributed to regeneration and release of total phosphorus from sediment into the water column by turbulence mixing (Chandran and Ramamoorthy, 1984). Phosphate exhibited highly significant seasonal variation ($p < 0.01$). In the present study, dissolved inorganic phosphate displayed significant positive correlation with salinity indicating the internal loading (Renjith et al., 2012).

The distribution pattern of salinity and silicate and their interrelationship in Cochin backwater system was investigated by (Anirudhan et al., 1987) and pointed out the fact that construction of Thanneermukkom bund had led to the stagnation of water resulting in the large changes in the hydrography. In the present study, both surface and bottom water exhibited higher silicate content during POM 08 and POM 10 (Figure 3.15). The maximum content was recorded at Aroor-Kumbalam (S6) (surface) during POM 09 and Eloor (S13) (bottom) during POM 09. Highly significant seasonal ($p < 0.01$) variation was noticed for silicate in the surface water of the study area. However, in bottom water, the significant spatial ($p < 0.05$) and seasonal ($p < 0.01$) variations were observed. Silicate exhibited significant negative correlation with salinity, suggesting its input through land runoff (Renjith et al., 2012).

Primary production can be limited by Fe availability in coastal environments (Kirchman et al., 2000; Bruland et al., 2001). Dissolved Fe in aquatic

systems can exist in two different oxidation states [Fe (II) and Fe (III)]. The Fe (III) is the thermodynamically stable form in oxygenated water and has a very low solubility in high saline water (Liu and Millero, 2002). Fe (III) becomes rapidly hydrolyzed into various Fe(III) oxyhydroxides. The low solubility of Fe oxyhydroxides and the tendency to form colloids which can contribute to the scarcity of directly bioavailable Fe species in the marine environment (Wen et al., 1999). Dissolved Fe (III) occurs for a major part as complexes (Fe (III)) with strong organic ligands (Waite, 2001). The majority of dissolved Fe in river water exists as small colloid particles (Wen et al., 1999). Flocculation of these colloids, upon mixing of fresh river water with seawater during estuarine mixing, causes a massive removal of the freshly formed particulate Fe (Sholkovitz, 1978). Riverine dissolved iron, comprises mostly colloidal iron oxy-hydroxides closely associated with natural organic matter (Nowostawska, 2008). Organic complexation is an important factor in the biogeochemistry of Fe in estuarine water, as it maintains iron in the dissolved phase at high salinities beyond the flocculation zone. The dissolved phase will be flushed from the estuary while the non-organically complexed fraction tends to aggregate and adsorb to particles, thereby exhibiting longer residence time (Morris et al., 1986). Organically complexed iron of estuarine systems can act as a source of dissolved iron for coastal water (Powell and Wilson-Finelli, 2003).

5. Conclusion

Values of pH in both surface and bottom water remained slightly alkaline at all the stations. Higher values for pH might be due to the influence of seawater ingression or increased photosynthetic activity. Wide fluctuations in the values of transparency might be due to discharge of water due to floating sediments carried by the river from catchment areas as well as dredging operations in Cochin estuary. Higher content for dissolved oxygen was recorded during monsoon, which could be due to the cumulative effect of higher wind velocity joined with heavy rainfall and the resultant freshwater mixing. The combined effects of higher biological production coupled with sinking of organic matter, discharge of untreated effluents, wastes from aquaculture fields and agricultural fields into the backwater system have contributed to the increased BOD levels in the study area. In the present investigation, no vertical stratification for salinity was observed and fresh water conditions were prevalent during the monsoon and the estimated higher values during post monsoon season could be due to increased rate of evaporation and sea water ingression. Among nutrients, ammonia displayed a non-uniform distribution throughout the entire study period which indicated an exogenic input in the estuary. The increased nitrate level was due to fresh

water inflow, organic decomposition and terrestrial run-off during the monsoon season. The lower contents of nitrite during premonsoon were due to less freshwater input, higher salinity, higher pH and also uptake by phytoplankton. The higher phosphate content in the water column could be attributed to regeneration and release of total phosphorus from sediment into the water column by turbulence mixing. Silicate exhibited significant negative correlation with salinity, suggesting its input through land runoff.

Anthropogenic activities like industrialization, urbanization and agricultural runoff have resulted in tremendous ecological stress on aquatic ecosystems. Analysis of variance revealed that spatial variation was highly significant ($p < 0.01$) in the case of nitrate. In the present study, NO_3^- was higher during POM 08 and POM 09 and recorded lower concentration during PRE 09 and PRE 10. The higher nitrate-N concentrations are related to more intense mixing of the super lying water column due to rain, land run off and high river discharges. The higher values were particularly important where there was influence on sediment from agriculture, industries and waste water and also physical degradation of the land area.

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