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## Seasonality in carbon chemistry of Cochin backwaters

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**Abstract:**

Seasonality in carbon chemistry of Cochin backwaters, Southern India, was investigated between 2018 and 2019. Dissolved inorganic carbon (DIC) showed strong seasonal variations. Lowest DIC was observed during the Southwest Monsoon (SWM), in conjunction with low salinity in surface waters, suggesting strong freshwater influence. The maximum concentration of partial pressure of carbon dioxide in water ( $p\text{CO}_2\text{w}$ ) was recorded from polluted waters of Vembanad Lake ( $\sim 16,000 \mu\text{atm}$ ). Excluding the SWM, the inner most stations (freshwater) showed lower  $p\text{CO}_2\text{w}$  levels compared with the outermost (estuarine) ones. With regard to sampling stations, all the environmental properties, except silicate and phosphate, exhibited significant variation, pointing to large spatial heterogeneity across the stations. Redundancy analysis suggested salinity to be inversely related to surface  $p\text{CO}_2\text{w}$ . High pH and low  $p\text{CO}_2\text{w}$  observed in some of the inner most stations indicates role of pH in carbonate speciation. Our study indicates large seasonal fluctuation in biogeochemical parameters and strong heterogeneity between individual stations which therefore necessitates development of local biogeochemical models for better understanding of carbon budget in these waters.

**Key words:** Vembanad Lake; carbon dioxide; Cochin; Dissolved Inorganic Carbon; Monsoon

## 1.0 Introduction

Although open oceans are known to act as a sink for atmospheric CO<sub>2</sub> (Takahashi et al., 2009), the role of estuaries still remains poorly understood (Borges et al., 2005, Cai et al., 2006; Pattanaik et al., 2020 and reference there in). Cai (2011) illustrated that estuaries are major land-ocean interaction zones where organic carbon (OC) and nutrients are processed, resulting in a high water-to-air carbon dioxide (CO<sub>2</sub>) flux ( $\sim 0.25 \text{ Pg C y}^{-1}$ ). For example, European estuaries have been found to emit between 30 and 60 million tons of carbon per year to the atmosphere, representing 5 to 10 % of the present anthropogenic CO<sub>2</sub> emissions for Western Europe (Frankignoulle et al., 1996). In comparison, measurements from the Indian sub-continent are sparse in space and time, making it difficult to delineate the annual budget. Mukhopadhyay et al. (2002), based on monthly variations in the Hooghly backwaters, found that the partial pressure of carbon dioxide in water (pCO<sub>2w</sub>) ranged from 220 to 1200  $\mu\text{atm}$ , and that it results in a flux of  $-3$  to  $84 \text{ mmol m}^{-2} \text{ d}^{-1}$  to the atmosphere. Surface pCO<sub>2w</sub> also exhibited large spatio-temporal variability in Mahanadi backwaters in eastern India, periodically changing from sink to source on an inter-annual basis (Pattanaik et al., 2020). A seasonal study of pCO<sub>2w</sub> in the Mandovi backwaters in western India revealed ranges between 110 and 2300  $\mu\text{atm}$  and a flux variation from  $-2$  to  $67 \text{ mmol m}^{-2} \text{ d}^{-1}$  to the atmosphere (Sarma et al., 2001). These studies suggest pCO<sub>2w</sub> variations are wider in Indian estuaries, which necessitates consistent and sustained scientific investigations over time to elucidate their collective role in emission of carbon dioxide to the atmosphere. Indian estuaries are influenced by monsoonal rainfall which modulates their runoff duration (Vijith et al., 2009). Therefore, strong gradients between wet and dry seasons are expected. In general, the pCO<sub>2w</sub> concentrations tend to be 4 – 5 times higher during wet seasons compared with dry seasons, with reported values ranging between 300 and 18,492  $\mu\text{atm}$  in Indian estuaries during the monsoon (Sarma et al., 2001; Gupta et al., 2008, 2009; Sarma et al., 2011; Sarma et al., 2012).

Backwaters of Kerala, situated in the southern peninsula of the Indian sub-continent, have witnessed rapid changes in their ecosystems due to anthropogenic perturbation in recent times (Gopalan et al., 1983; Martin et al., 2011 and references therein). Although considerable attempts have been made to understand the physico-chemical properties in this region, the

seasonal dynamics of  $p\text{CO}_2\text{w}$  remains poorly quantified (Gandhi et al., 2011; Gupta et al., 2009). Gupta et al. (2009) illustrated that the Cochin backwaters can sustain high levels of  $p\text{CO}_2\text{w}$  (up to  $6000 \mu\text{atm}$ ) and  $\text{CO}_2$  effluxes (up to  $274 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ); especially during monsoons, based on the data collected in the year 2005. Sarma et al. (2012) studied 27 estuaries along the Indian coast and showed that  $p\text{CO}_2\text{w}$  can range between  $\sim 300$  and  $18,492 \mu\text{atm}$  during monsoons. Martin et al. (2011), highlighted significant eutrophication in Cochin backwaters due to possible urbanization and associated nutrient influx, with chlorophyll-*a* (Chl-*a*) concentrations increasing six-fold in the study period, in comparison with the previous decade. However, though earlier published results from the backwaters go back to 2005 (Gupta et al., 2009), analysis of the changes in surface  $p\text{CO}_2\text{w}$  recently has not been attempted. Bhavya et al. (2016) showed primary productivity within the Cochin backwaters to be higher than those in other comparable coastal sites from India, which is attributed to the consistent supply of nutrients within the backwaters, presumably through anthropogenic and agricultural runoff. As changes in aquatic carbon chemistry is also tightly coupled with local productivity and remineralisation processes therefore some changes when compared with the study conducted in 2005 is expected. Further, Cochin backwaters also show strong seasonal gradients in temperature and salinity distribution (See review by Menon et al., 2000) which may also influence the surface  $p\text{CO}_2\text{w}$ , due to solubility effects (Takahashi et al., 1993). Hence, for a region where both physical and biological processes modulate seasonally, periodic investigations, along with comparison of past reports, are important to delineate the effect of urbanization on aquatic ecosystems, and to identify trends in  $p\text{CO}_2\text{w}$ .

Thus, the objective of the present study is to evaluate the seasonal dynamics in aquatic carbon properties from the polluted backwaters of Cochin, Southern India, and understand its seasonal drivers.

## 2. Methodology

### a) *Experimental approach:*

Our observations are based on new datasets generated during 2018 - 2019 covering Southwest Monsoon (SWM) which include June, July and August months of 2018; Fall Inter-Monsoon (FIM), which include September, October and November 2018; and Northeast Monsoon (NEM) wherein sampling were carried out during December 2018, January and February of, 2019. Further, we also compare our datasets with past observations, to understand the influence of anthropogenic perturbations during the past decade, on the aquatic inorganic carbon pool and associated biogeochemical properties in this region.

### b) *Brief description of the study area*

The Cochin backwaters is situated between the latitudes  $\sim 9.50^{\circ}\text{N}$  -  $10.10^{\circ}\text{N}$  and longitudes  $76.10^{\circ}\text{E}$  -  $76.50^{\circ}\text{E}$ , along the southwest coast of India, extending parallel to the coast from Munambam in the north to Alappuzha in the south, in the state of Kerala. The length of this narrow water body is  $\sim 113$  km, while the width varies from 14.5 km at its widest part to a few hundred meters. The bathymetry varies from 1.5 m to 6 m in the entire backwaters except in the active shipping channel where the depth is maintained at 10 – 13 m by dredging (Menon et al., 2000). Circulation in this region predominantly follows the tidal regime: it is mixed semi-diurnal in nature, with an average tide height of  $\sim 1$  m (Qasim and Gopinathan, 1969; Srinivas et al., 2003; Shivaprasad et al., 2013). In general, the incursion of saline waters is observed during the flood tide and vice-versa during the ebb tide. The intrusion of saline water is subdued during the SWM due to the heavy monsoon-induced efflux of freshwater into the backwaters, restricting the saline waters to the deeper layers of the backwaters. Hydrography of these waters is significantly influenced by the intrusion of seawater and river discharge, which is, in turn, regulated by the SWM.

### c) *Measurements of biogeochemical parameters in and around Cochin back waters*

A total of 13 stations were sampled during various seasons between 2018 and 2019, in and around Vembanad Lake within the Cochin backwaters (Figure 1). Samples were collected during SWM, FIM and NEM. A factory-calibrated SeaBird Electronics (SBE) 9/11 + Conductivity-Temperature-Depth profiler (CTD) with Fluorescence sensor (a proxy for Chl-*a*

hereafter) was used at all locations to record vertical profiles in these properties. Water samples were collected from 1 m below the surface with a Niskin sampler attached to a Nylon rope. The water samples for dissolved oxygen (DO) were collected first, followed by pH, dissolved inorganic carbon and nutrients. DO samples were immediately fixed and then analyzed back in the laboratory by Winkler's method as modified by Grasshoff (1983). The uncertainties in DO measurements from replicates were  $< \pm 0.01 \text{ mg l}^{-1}$ . Samples for DIC and nutrients were treated with saturated mercuric chloride as per the standard oceanographic protocol (US JGOFS) and analyzed at the biological oceanographic laboratory of the National Remote Sensing Centre, Hyderabad, India. The accuracy of DIC was  $\pm 2 \text{ } \mu\text{mol kg}^{-1}$  for this study based on replicate measurements of Certified Reference Material (CRM) batch number 170 purchased from Dickenson Laboratory, Scripps Institute of Oceanography, San Diego, USA, further detailed in protocol of (D.O.E. 1991). Further, variations in laboratory accuracy relative to the certified value of the reference material, for the period 2018-2019 ( $\pm 3.4 \text{ } \mu\text{mol kg}^{-1}$ ) are also presented as supplementary figure S1. Inorganic nutrients (nitrate, silicate, and phosphate) were determined by standard spectrophotometric methods (Grasshoff et al., 1999) using Skalar Autoanalyser (San ++). Uncertainties due to multiple measurements of replicate samples for nutrients were  $< \pm 0.1 \mu\text{mol l}^{-1}$  based on CRM 170. pH was measured using Metrohm pH meter and had an accuracy of  $\pm 0.002$  units. The measured values on NBS scale were first converted to *in situ* pH and then to total scale. The  $\text{pCO}_2\text{w}$  values were computed using measured salinity, temperature, pH, dissolved inorganic carbon and nutrients (phosphate and silicate) using  $\text{CO}_2\text{SYS.EXE}$  software (Lewis and Wallace 1998). The dissociation constants  $K_1$  and  $K_2$  were used according to Peng et al. (1987). With these precision values of DIC and pH, the expected error in the  $\text{pCO}_2\text{w}$  calculation is found to be  $< 10 \text{ } \mu\text{atm}$ .

#### d) Statistical Analyses

The environmental data were subjected to two-way ANOVA to determine whether the carbon measurements varied significantly across stations and sampling periods. A  $p$  value  $\leq 0.05$  was considered to be significant. Pearson correlation analysis was performed with XLSTAT version 7.5.2. Pearson correlation produces a sample correlation coefficient,  $r$ , which measures the strength and direction of linear relationships between pairs of continuous

variables. Redundancy analysis (RDA) was carried out to understand the relationships between explanatory variables and response variables using Canoco 4.5. RDA results are expressed in biplots, wherein the relationships between different environmental variables are the function of length, direction of orientation and angle between the variables. RDA is a direct gradient analysis technique which uses linear relationships between components of response variables that is "redundant" with a set of explanatory variables. RDA extends multiple linear regressions (MLR) by allowing regression of multiple response variables on multiple explanatory variables as detailed later.

### 3. Results and Discussion

In this study, station 1 (outermost) is located at the bar mouth region (Figure 1) with a depth between 5 to 8 m. This is the region where high level of exchange of estuarine waters takes place with the adjacent coastal oceans. It also shows strong tidal influence (Menon et al., 2000), and is located adjacent to a deep shipping channel with regular ship movement. It is a major transit zone between two islands, namely Vypin and Fort Kochi. Both the islands as well as nearby regions of this station are densely populated, with heavy sewage and waste water discharge from households and fish processing units; pollution from container and passenger ships is also seen occasionally. The innermost stations (11 to 13) are in the vicinity of agricultural fields where runoff during SWM is expected. Station 13 is situated in the southernmost extent of Vembanad Lake; the water here is very shallow compared with the other stations. Agriculture and aquaculture are the dominant activities observed around Station 13.

The seasonal changes in temperature distribution were within 3 °C, with lowest mean surface temperature 27.4 °C being recorded during SWM (Figure 2). During FIM the stations (9 to 13) recorded ~ 2 °C higher temperature compared to the outer most stations (1 to 5) and showed similar values during NEM. Similarly, the average surface salinities were lowest during SWM and highest during NEM. A sharp salinity change was observed between station 1 and 13 (Figure 2). Salinities close to 1 psu were occasionally recorded at the inner most stations suggesting strong freshwater influence. This is consistent with the trend in oxygen



data observed during the investigation (Figure 2). The average surface oxygen concentrations were lower during SWM at all stations compared with other seasons (Figure 2), and followed similar seasonal distribution like with temperature (Figure 2). In contrary, the highest oxygen concentrations occurred in FIM followed by NEM. Station-wise, lower salinity values were observed at the innermost stations influenced by riverine inputs (stations 11 to 13) where salinity remained  $< 2$  psu throughout the study period. The lowest surface oxygen observed during the SWM is associated with the large runoff from agricultural lands received by most of the inner most stations sampled (Stations 11 to 13). Gupta et al. (2009) reported strong under saturation with respect to oxygen concentrations during SWM, which is consistent with relatively low oxygen values observed during this investigation (Table 1). In general, the stations with lower salinity (innermost stations 7 to 13, where maximum salinity is observed to be a little above 11 psu between December and January) showed higher oxygen concentrations, presumably due to effect of salinity on oxygen solubility (Figure 2) (Sarmiento and Gruber, 2006).

The seasonal dynamics associated with dissolved inorganic carbon, chlorophyll a, pH and  $pCO_2w$  from Cochin backwaters are illustrated in Figures 3 & 4. The dissolved inorganic carbon (DIC) showed strong seasonal variability and followed the salinity pattern (Figure 2 & 3). This is also corroborated by the strong positive correlation observed between salinity and DIC during this investigation ( $r = 0.884$ ;  $p < 0.05$ ). For example, fresh water salinity of 0.1 psu at station 13 was associated with a DIC of  $278 \mu\text{mol kg}^{-1}$ . Similarly, the highest DIC ( $2103 \mu\text{mol kg}^{-1}$ ) was reported from station 1, characterized by pH of 8.10, reflecting the influence of seawater. The lowest DIC was associated with SWM, whereas the highest was observed during NEM. The DIC in the river end station (13) was significantly less than the global average of  $720 \mu\text{mol kg}^{-1}$  (Meybeck, 1982). However, it was consistent with data reported from other estuaries in India (Sarma et al., 2001; Sarma et al., 2012). Gupta et al. (2009) showed rivers entering the Cochin backwaters had DIC in the range of  $162 - 332 \mu\text{mol kg}^{-1}$ . We found a conspicuous difference in DIC values between stations close to the bar mouth (1 to 7) and stations influenced by riverine inputs (8 to 13). Irrespective of the seasons, the innermost stations showed lower dissolved inorganic carbon values  $< 600 \mu\text{mol kg}^{-1}$ . This effect is due to influx of river water (conservative behavior) which generally has low DIC. In

contrast, both lowest and highest pH values were recorded within the innermost stations (Figure 4). For example, station 10 recorded a pH of 5.59 units during the SWM whereas the highest pH was associated with station 12 (8.69 unit) during FIM. Station 1 which acts as an exchange point between estuarine and coastal waters recorded a pH range between 6.60 to 8.18 units. The lowest mean pH across all stations (6.73 unit) was also associated with the SWM. It should be noted that the discharge of agricultural runoff into the estuarine system is generally rich in humic acids and complex dissolved organic carbon, which can significantly lower pH levels. This is consistent with the distribution of surface Chl-*a* observed during this investigation (Figure 4). The lowest mean Chl-*a* ( $5.8 \mu\text{g l}^{-1}$ ) was associated with the monsoon seasons, presumably due to large sediment load and low sunlight levels in the backwaters and the highest Chl-*a* was associated with NEM across all stations sampled. In general the inner most stations had higher chlorophyll compared to the stations (1 to 5) during SWM however significant increase in middle stations were observed during FIM and NEM. SWM was also associated with high nutrient concentrations within the backwaters, which clearly suggest strong anthropogenic runoff in the Cochin backwaters (Figure 5). Further a gradual increase in the surface chlorophyll from SWM to NEM suggests modest change in primary productivity in the water column with seasons. It is likely that more stable water column and low river runoff during post monsoon could trigger such changes. Temperature and salinity showed significant positive correlation with surface chlorophyll suggesting influence of physical factors in controlling phytoplankton distribution in the region during non monsoon periods (Table 4). On the contrary, lowest nutrient values were associated with NEM. Nitrate concentrations were relatively higher at the outermost stations close to coast compared to inner ones. However drastic seasonal decrease was observed during FIM and NEM. A similar seasonal gradient was observed with respect to silicate. Some of the highest silicate concentrations observed was associated with the SWM (Figure 5) which showed gradual decrease thereafter. In contrary, the phosphate was found to be more abundant during FIM and NEM with higher values associated with the inner most stations. This difference of presence of phosphate in the water column relative to other two macronutrients presumably reflects agricultural contribution. It is imperative that the agricultural fields associated with the inner most stations will be more active during FIM and NEM therefore contribution of fertilizer cannot be ignored. The magnitude of the nutrients observed in the Cochin

backwaters is well comparable with values reported from other Indian estuaries (Sardessai et al., 1993; Sarma et al., 2001, 2012). Further, increase in pH ( $> 8.40$  unit) at the innermost stations during non-monsoon seasons is presumably reflects the use of fertilizers, which are known to increase the pH levels in other Indian estuaries (Sarma, 2001). In contrast, these stations were associated with very low  $p\text{CO}_2\text{w}$  levels ( $< 300 \mu\text{atm}$ ) (Figure 5), most likely due to the influence of alkaline waters on carbonate speciation where  $[\text{CO}_3^{2-}]$  tends to dominate at higher pH. Excluding SWM, the innermost stations (8 to 13) showed lower  $p\text{CO}_2\text{w}$  levels compared with stations 1 to 7 throughout the sampling period. This suggests strong spatio-temporal heterogeneity and patchy distribution of  $p\text{CO}_2\text{w}$  within the Cochin backwaters, which has not been reported earlier. Station 2 recorded the highest concentration of  $\sim 16,000 \mu\text{atm}$  and was associated with NEM, followed by Station 1. Gupta et al. (2009) reported that bacteria-mediated mineralization of organic matter is mainly responsible for the build-up of  $p\text{CO}_2\text{w}$  and increased  $\text{CO}_2$  emission to the atmosphere, indicating the relevance of heterotrophy in modulating  $p\text{CO}_2\text{w}$  values in the Cochin backwaters. The monsoonal concentration of  $p\text{CO}_2\text{w}$  at Station 1 (mixing zone) ranged between 252 and 5339  $\mu\text{atm}$ ; it was relatively lower during the rest of the seasons. A comparison with historical datasets from the Bar Mouth station (maximum mixing zone) is presented in Table 2. Interestingly, a modest increase of 184  $\mu\text{atm}$  in surface  $p\text{CO}_2\text{w}$  was observed when compared with published data from Southwest Monsoon of 2005. Gupta et al. (2009) had undertaken a comprehensive study of surface  $p\text{CO}_2\text{w}$  distribution along the Cochin backwaters, therefore his data sets from 2005 is appropriate for comparison. However our seasonal variability is much larger in comparison to the modest increase we observed at this station. Further, the DIC concentrations reported from sampling carried out in 2012 (Bhavya et al., 2018) is largely similar to the 2018 values in the present study (Table 2). Our analysis suggests not much change with respect to aquatic carbon properties within the mixing zone (estuarine mouth) with respect to the SWM concentrations during the last decade and observed changes therefore reflects inter annual variability.

#### 4. Statistical Analysis

With regard to sampling stations, all the environmental properties, except silicate and phosphate, exhibited significant variation, pointing to the spatial heterogeneity across the stations (Table 3). All the environmental variables, except  $p\text{CO}_2$ , showed significant variation across sampling periods, indicating the influence of monsoon patterns as a pivotal regulatory factor (Table 3). Further, Pearson correlation analysis showed salinity to be positively correlated with DIC (Table 4) suggesting coastal waters as an important source of DIC within the Cochin backwaters which is consistent with the global estuarine DIC distribution. Results of RDA suggest DIC shows some weak positive influence on surface  $p\text{CO}_2$  whereas salinity suggests inverse relations which clearly indicate the low saline waters were associated with high  $p\text{CO}_2$ .

## 5. Summary

Seasonal dynamics of aquatic carbon parameters from Cochin, backwaters, Southern India were investigated between 2018 and 2019. The lowest DIC was observed during SWM in conjunction with low oxygen in surface waters, suggesting strong freshwater influence. The DIC for the riverine end member was significantly less than the global average. It was, however, consistent with data reported from other estuaries in India. The maximum concentration of  $\sim 16,000 \mu\text{atm}$  was recorded from the northern part of the Vembanad Lake. Excluding the SWM, the freshwater stations showed lower  $p\text{CO}_2$  levels, with corresponding high pH values, compared with the outermost stations. These suggest strong spatial heterogeneity and patchy distribution of the aquatic carbon parameters within the Cochin backwaters. Salinity showed a strong correlation with dissolved inorganic carbon within the Cochin backwaters. Our analysis does not suggest significant change with respect to the aquatic carbon parameters during the last decade. However, the response of the coastal ecosystem to the nutrient load brought in by the Cochin backwaters, remains to be fully evaluated.

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**Authors' Contribution**

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➤ MVR Shesha Sai, Saroj Bandhu Choudhury, P V Nagamani, Rajdeep Roy: wrote the scientific proposal and secured the funding from ISRO, Dept. of Space, Govt. of India

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➤ Pranav P, Sajhunneesa Tirunilath; Anas Abdulaziz; Rajdeep Roy: carried out the seasonal samplings; measurements of samples and made the figures for the manuscript.

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➤ Rajdeep Roy; Grinson George; Chiranjivi Jayaram; Priya M D'Costa; Nandini Menon: did the data interpretation and wrote the paper.

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➤ Shubha Sathyendranath gave the overall guidance and revised the draft manuscript.

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**Table 1:** Mean  $\pm$  SD and range of physico-chemical parameters at different locations of Cochin backwaters observed during three different seasons between 2018-19.

| Parameters                    | South West Monsoon<br>(June-August 2018) |             | Fall Inter Monsoon<br>(September- November<br>2018) |             | North East Monsoon<br>(December 2018-February<br>2019) |             |
|-------------------------------|------------------------------------------|-------------|-----------------------------------------------------|-------------|--------------------------------------------------------|-------------|
|                               | Mean $\pm$ SD                            | Range       | Mean $\pm$ SD                                       | Range       | Mean $\pm$ SD                                          | Range       |
| Temperature                   | 27.41 $\pm$ 0.69                         | 25.97-28.36 | 29.73 $\pm$ 0.95                                    | 27.89-30.96 | 29.96 $\pm$ 0.878                                      | 28.30-31.14 |
| Salinity                      | 0.35 $\pm$ 0.59                          | 0.05-2.12   | 2.05 $\pm$ 2.91                                     | 0.04-8.42   | 10.36 $\pm$ 9.81                                       | 0.24-29.19  |
| Chl-a                         | 5.84 $\pm$ 2.26                          | 2.78-10.03  | 7.45 $\pm$ 3.76                                     | 2.1-13.46   | 9.74 $\pm$ 5.11                                        | 3.93-19.24  |
| DIC                           | 357 $\pm$ 104                            | 226-647     | 451 $\pm$ 261                                       | 143-1053    | 764 $\pm$ 567                                          | 129-1887    |
| pH                            | 6.73 $\pm$ 0.15                          | 6.32-6.96   | 8.24 $\pm$ 0.40                                     | 7.33-8.70   | 7.73 $\pm$ 0.45                                        | 6.59-8.19   |
| SiO <sub>4</sub> <sup>-</sup> | 37.5 $\pm$ 6.36                          | 23.95-49.07 | 36.20 $\pm$ 8.70                                    | 24.30-49.30 | 12.10 $\pm$ 3.15                                       | 7.85-19.6   |
| PO <sub>4</sub> <sup>-</sup>  | 1.32 $\pm$ 1.32                          | 0.02-4.75   | 1.59 $\pm$ 0.62                                     | 0.97-3.19   | 1.93 $\pm$ 0.82                                        | 0.63-3.47   |
| NO <sub>3</sub> <sup>-</sup>  | 14.2 $\pm$ 6.93                          | 3.86-28.4   | 9.95 $\pm$ 5.09                                     | 4.23-24.2   | 3.43 $\pm$ 3.04                                        | 0.54-9.89   |
| DO                            | 6.74 $\pm$ 0.25                          | 6.25-7.13   | 7.25 $\pm$ 0.25                                     | 6.82-7.70   | 7.02 $\pm$ 0.32                                        | 6.51-7.38   |
| pCO <sub>2w</sub>             | 1596 $\pm$ 1591                          | 217-6161    | 482 $\pm$ 361                                       | 168-1290    | 738 $\pm$ 832                                          | 139-16511   |

**Table 2:** The table reflects the comparison of water quality with respect to oceanic carbon parameters in rivers entering the Cochin backwaters (Stn 1, Bar Mouth) with historical data during of Southwest Monsoon.

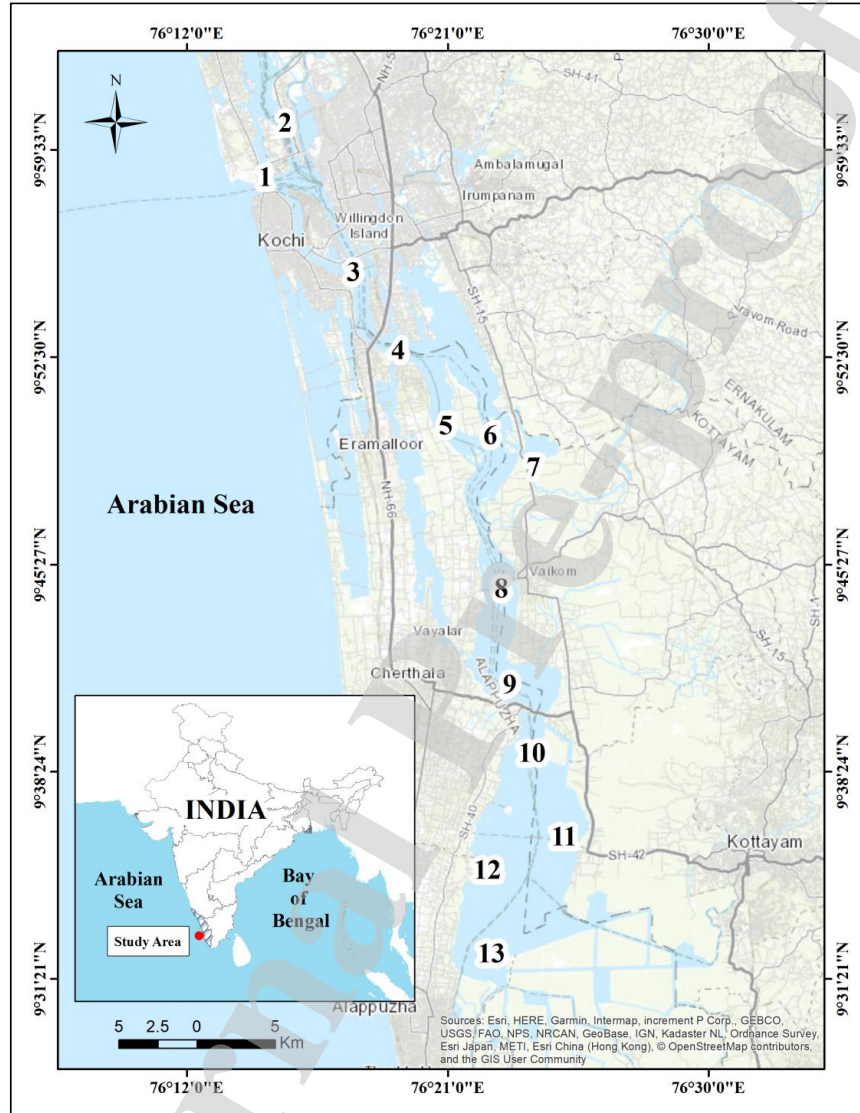
| Reference                                   | Sampling period                                               | DIC ( $\mu\text{mol kg}^{-1}$ ) | pH    | Chl- <i>a</i> ( $\mu\text{g l}^{-1}$ ) | pCO <sub>2</sub> ( $\mu\text{atm}$ ) |
|---------------------------------------------|---------------------------------------------------------------|---------------------------------|-------|----------------------------------------|--------------------------------------|
| This Study (SWM average)                    | June–July–August (SWM)                                        | 647                             | 6.80  | 6.26                                   | 3037                                 |
| Gupta et al., (2009)<br>(northern stations) | Monsoon- September 2005(summer monsoon)                       | 413                             | 6.657 | 6.08                                   | 2853                                 |
|                                             | Early Monsoon April 2005 (Late pre monsoon + heavy rain fall) | 1192                            | 7.280 | 16.7                                   | 2043                                 |
| Sarma et al., 2012                          | 28th July to 18th August 2011                                 | 455                             | 7.11  | NA                                     | 1804                                 |
| Bhavya et al., 2017                         | Monsoon 2012, St-3(Bar mouth)                                 | 623                             | 7.192 | 3.05                                   | NA                                   |
| Vishnu et al., 2018                         | June-September, 2015- Bar mouth                               | NA                              | 8     | 3.74                                   | NA                                   |
| Madhu et al., 2010                          | June, July, August, and September 2006                        | NA                              | NA    | Surface-13.7<br>Bottom- 9.6            | NA                                   |

**Table 3.** Results of the two-way ANOVA to analyze the variation in different environmental parameters across stations and sampling periods.

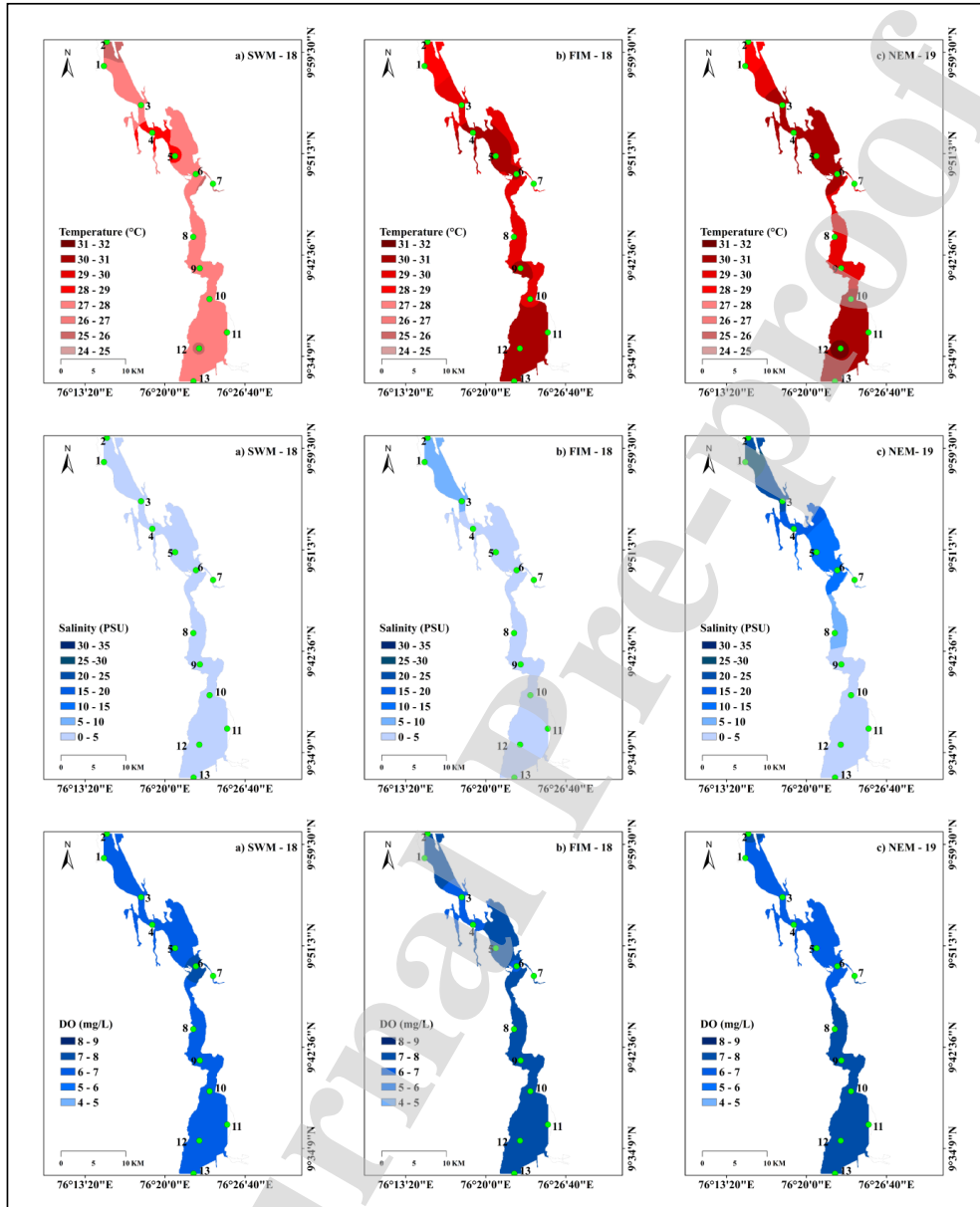
| Parameters                                | Variation across sampling periods<br>(p) | Variation across stations<br>(p) |
|-------------------------------------------|------------------------------------------|----------------------------------|
| Temperature                               | 1.39E-32                                 | <0.001                           |
| Salinity                                  | 6.04E-14                                 | <0.001                           |
| DO                                        | 2.63E-22                                 | 0.0026                           |
| Chl-a                                     | 7.67E-06                                 | 0.0056                           |
| DIC                                       | 1.89E-06                                 | <0.001                           |
| pH                                        | 8.91E-27                                 | 0.0003                           |
| Silicate                                  | 5.93E-24                                 | 0.0818                           |
| Phosphate                                 | 0.0005                                   | 0.1292                           |
| Nitrate                                   | 6.05E-11                                 | 0.0004                           |
| pCO <sub>2</sub>                          | 0.1300                                   | 0.0005                           |
| Significant values are shown in red font. |                                          |                                  |

**Table 4:** Pearson Correlation matrix for physico-chemical variables measured around Cochin backwaters for the period 2018-2019. (Bold values indicate correlation is significant at  $p < 0.05$ ).

| Correlation matrix: | Temp          | Sal           | PO <sub>4</sub> | SiO <sub>3</sub> | pH    | DIC   | Chl-a |
|---------------------|---------------|---------------|-----------------|------------------|-------|-------|-------|
| Temp                | 1             |               |                 |                  |       |       |       |
| Sal                 | 0.124         | 1             |                 |                  |       |       |       |
| PO <sub>4</sub>     | -0.003        | <b>0.330</b>  | 1               |                  |       |       |       |
| SiO <sub>3</sub>    | <b>-0.289</b> | <b>-0.288</b> | <b>-0.217</b>   | 1                |       |       |       |
| pH                  | <b>0.578</b>  | 0.039         | 0.003           | -0.088           | 1     |       |       |
| DIC                 | 0.104         | <b>0.882</b>  | <b>0.327</b>    | -0.164           | 0.106 | 1     |       |
| Chl-a               | <b>0.316</b>  | <b>0.247</b>  | 0.128           | -0.021           | 0.047 | 0.085 | 1     |

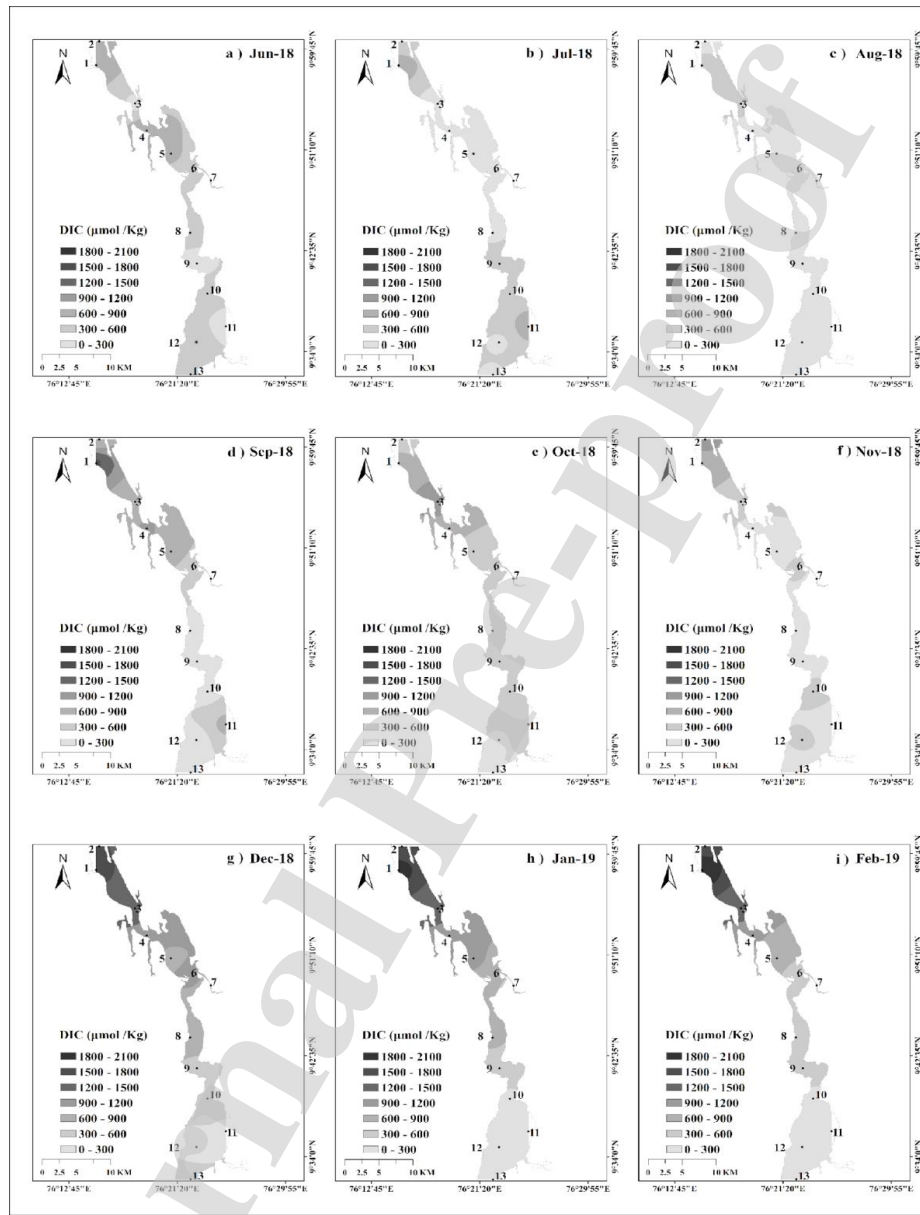


**Figure 1:** Station locations in the Cochin backwaters region, sampled during 2018-2019.

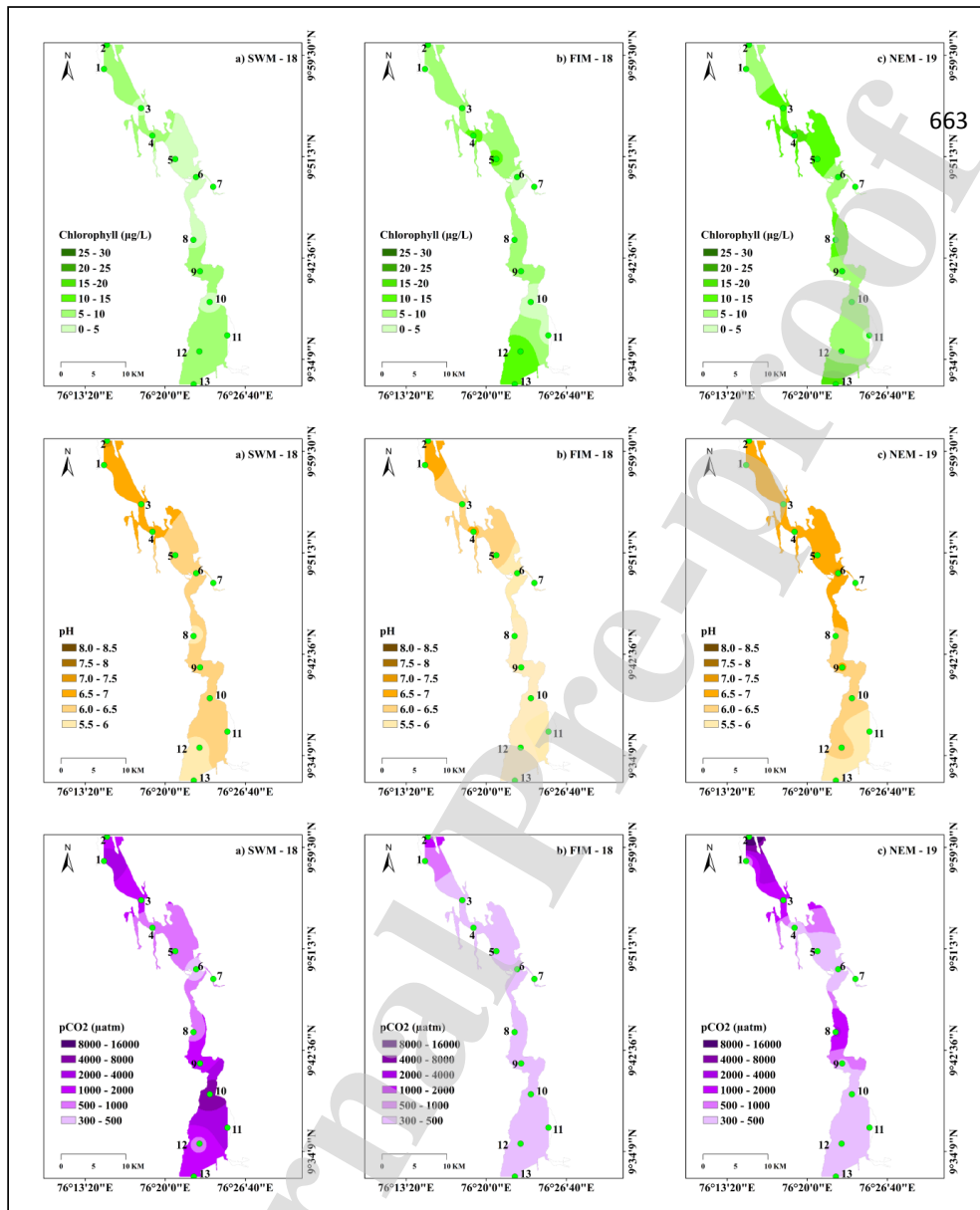


**Figure 2:** Seasonal changes observed in surface temperature in (°C), Salinity (psu) and oxygen (mg/L) along 13 stations in Cochin backwaters during the year 2018-2019.



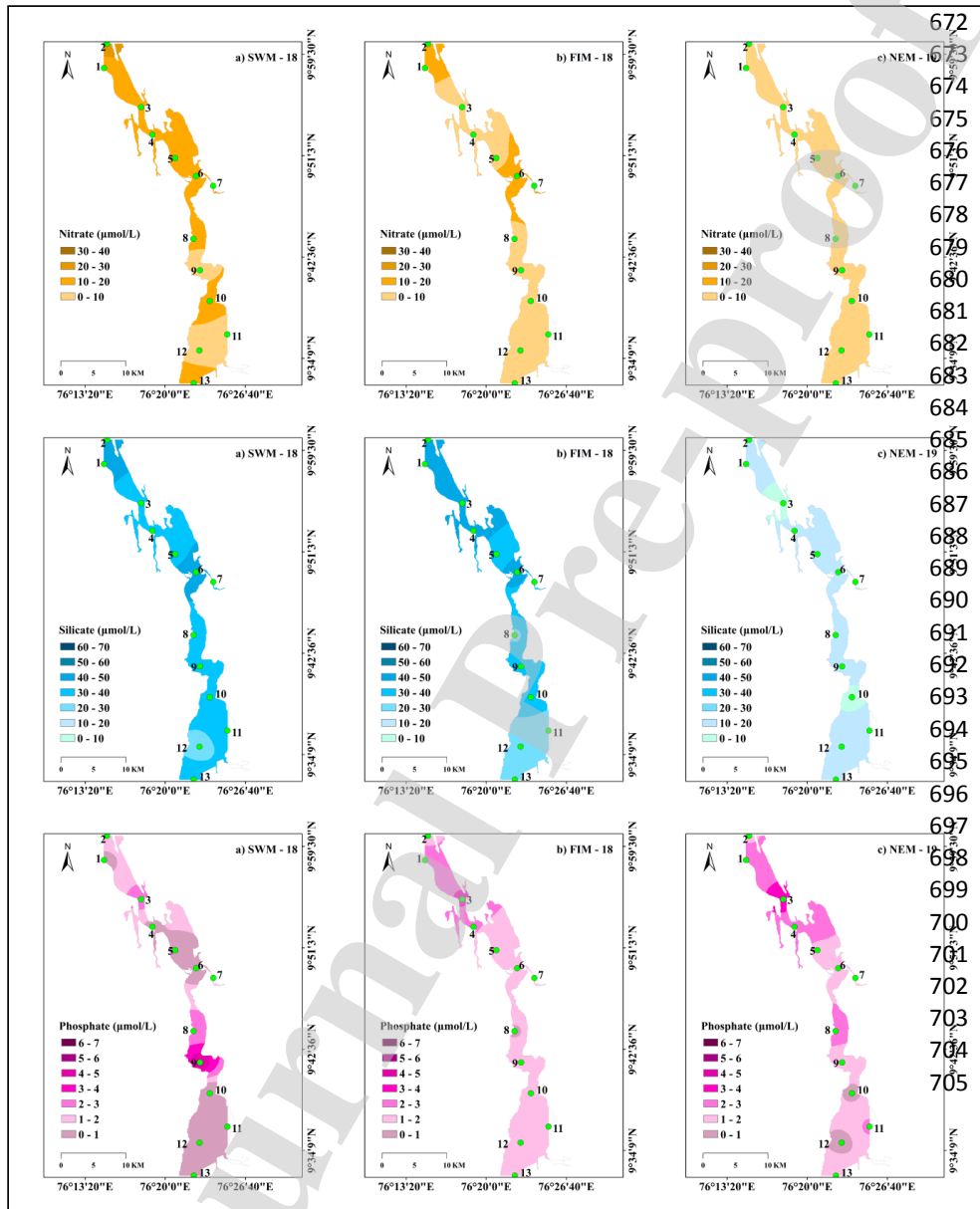


**Figure 3:** Seasonal changes observed in of dissolved inorganic carbon (DIC) of surface waters in ( $\mu\text{mol kg}^{-1}$ ) along Cochin backwaters during the year 2018-2019.

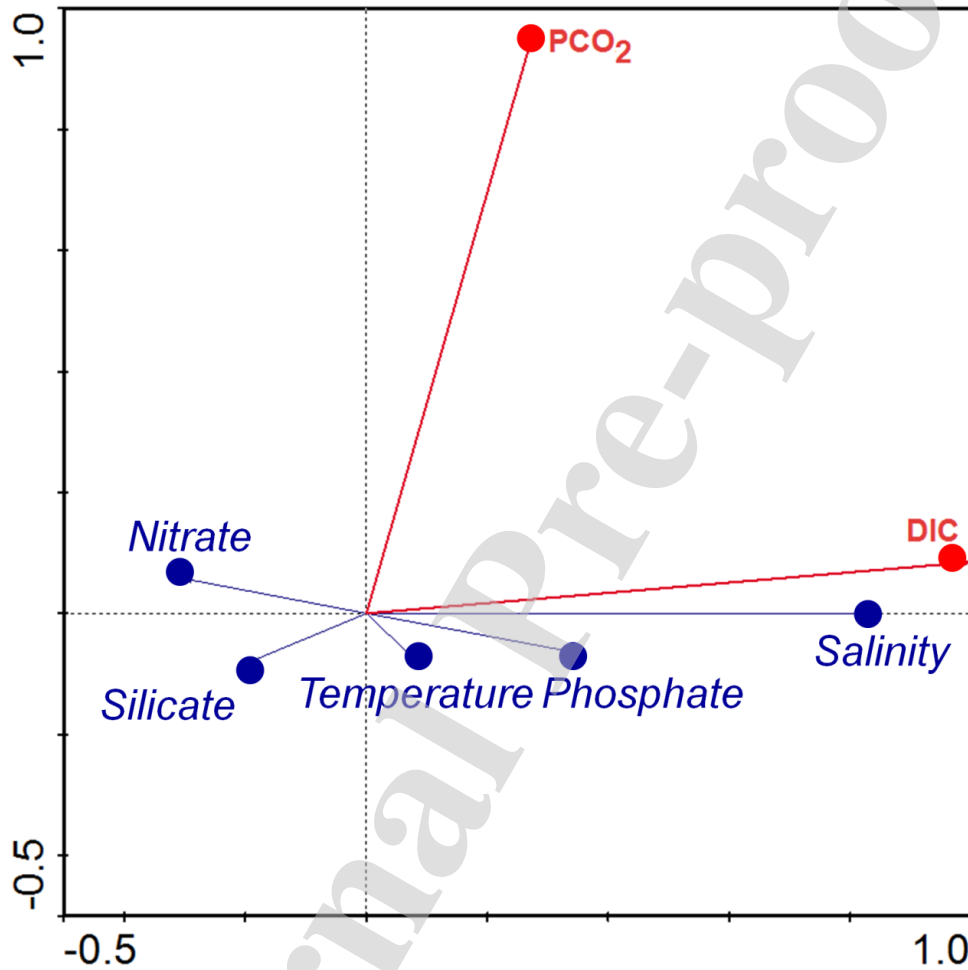


**Figure 4:** Seasonal changes associated with surface chlorophyll in ( $\mu\text{g/L}$ ); surface pH and surface waters pCO<sub>2w</sub> ( $\mu\text{atm}$ ) from Cochin backwaters. Sharp increase in concentrations in pCO<sub>2w</sub> is noted during July. Thereafter, there is significant decrease and distribution becomes patchier. In contrary surface chlorophyll was more abundant during NEM.

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**Figure 5:** Seasonal changes associated with surface nutrients distribution ( $\mu\text{mol/L}$ ) along Cochin backwaters during the year 2018-2019. Note silicate and nitrate were more abundant during the SWM and shows gradual decrease trend thereafter.



**Figure 6:** Representation of bi plot showing the results of the Redundancy Analysis (RDA). The angles between all vectors reflect their (linear) correlation. The correlation is equal to the cosine of the angle between vectors. As per the analysis DIC and nitrate seems to suggest some influence in surface  $\text{pCO}_2$  in this region.

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: