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Partial pressure of carbon dioxide (pCO$_2$) and air-water CO$_2$ exchange in the tropical semidiurnal estuarine system

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Time-series observations of the Vellar estuary between May 2013 and December 2019 showed clear variability with respect to space and time in the distribution of nutrients, partial pressure of carbon dioxide (pCO$_2$) and air-water CO$_2$ exchange. Lower and higher salinities revealed significant seasonality in estuarine pCO$_2$, as well as variations in the seasonal pattern due to the freshwater discharges during monsoon rainfall. The pCO$_2$ attained the highest levels (8457 μatm) during monsoon which coincided with the lowest pH (7.498) and the undersaturation of pCO$_2$ (322 μatm) was observed with maximum pH (8.182) during pre-monsoon. The Principal Component Analysis (PCA) identified four components that accounted for 77.28 % of the total variance and explained the significant influence of nutrients, chlorophyll and temperature on pCO$_2$ distribution. Similarly, the multiple linear regression analysis showed significant influence of environmental variables on pCO$_2$ variability with a R^2 of 0.957, SEE±230.816, $p < 0.001$. The surveyed area of the Vellar estuary had an overall pCO$_2$ of 1068 μatm and was supersaturated with regard to the atmospheric pCO$_2$ throughout the year, with an average CO$_2$ flux of 4.13±5.59 mmol C m^{-2} d^{-1} to the atmosphere. During the study period, the Vellar estuary actively supplied 650.2 mol C m^{-2} Y^{-1} to the atmosphere. Hence, the metabolic balance of the estuarine ecosystem is aided by land derived organic carbon accompanied with freshwater flows from the Vellar river, constituting the estuary as a substantial source of atmospheric CO$_2$.

[**Keywords**: Air-water CO$_2$ flux, Dissolved Inorganic Carbon (DIC), Nutrients, pCO$_2$, Total Alkalinity (TA), Vellar estuary]

Introduction

Coastal regions, particularly tidal estuaries, contribute significantly in carbon transfer and transformation from the land to the neighbouring coastal zone. Carbon dioxide is a significant greenhouse gas that has a significant impact on the biogeochemistry of estuaries and adjacent coastal waters. Among them, estuaries gained attention as they are the bio-geochemically most active areas[1]. Coastal waters, which account for only 7.6 % of the world's ocean surface area[2], have an important part in the net absorption of atmospheric CO$_2$ through a rapid biological production. Estuaries are inextricably tied to the organic carbon pool via photosynthesis and respiration, which are highly impacted by the terrestrial nutrient fluxes and labile carbon, which are tightly correlated to the organic carbon cycle via carbon dioxide consumption and production[3].

Natural carbon flow from rivers to the ocean is around 0.8 Pg C Y^{-1}, with half of it is organic and the remainder inorganic, while human impact contributes approximately 0.1 Pg C Y$^{-1(\text{ref. }4)}$. Organic carbon is generally made up of plant detritus and phytoplankton, whereas inorganic carbon is mostly made up of soil and rock erosion, as well as microbial oxidation of organic matter[5]. Carbonaceous particles from river run-off settle, degrade, and leave carbon back into the estuarine and coastal system.

The net internal organic metabolism and physical mixing influenced by external inputs from the land and ocean determine the partial pressure of carbon dioxide (pCO$_2$) in the estuary-plume. Almost all estuaries have been discovered to be a source of CO$_2$ to the atmosphere[6-8]. Unlike the open seas, which operate as a net absorber of atmospheric CO$_2$, the contribution of coastal waters to the global CO$_2$ fluxes is uncertain due to lack of data for major portions of the coastal zones[9].

Estuaries are defined by the mixing of turbid, nutrient-rich, and coloured river discharge with comparably clear, nutrient-poor ocean water, resulting in a salinity, nutrient availability, and light in continuum[10]. Most of the Indian estuaries are seasonal estuaries characterised with bulk riverine runoff during monsoon periods and exhibit non-steady state behaviour[11]. At those times the total volume of monsoonal discharges far exceeded by the peak discharge period and the entire estuary resembles riverine condition[12]. During the rainy season, these estuaries exhale 4 – 5 times more CO_2 than during the dry season[9]. The pCO_2 levels are registered highest in the Indian estuaries as > 30,000 μatm in the Mandovi-Zuari estuary[6], Godavari estuary[12], Cochin estuary[13], and Chilka estuary[14] with corresponding lower pCO_2 levels during the dry periods in all these estuaries.

There has been little research on the biogeochemistry of the Indian subcontinent's major rivers and estuaries. No such studies are available for Vellar estuary until now, a classical semidiurnal estuarine system influenced by seasonal river discharges. As a result, the goal of this study is to investigate the link between environmental parameters influencing the distribution of carbon dioxide partial pressure and the air-water flux of CO_2 from the estuary to the atmosphere and the nearby coastal zone.

Materials and Methods

Study area

Vellar river meets the Bay of Bengal at Parangipettai after forming an estuarine system. The Vellar river flows from the foothills of Servarayan in Salem for 480 kilometres before emptying into the Bay of Bengal[15]. The breadth of the estuary is 200 meters with a maximum depth of 5 meters and the tidal range is about one meter. Due to the availability of excessive nutrients, this estuary is supporting high biological production. Five sampling stations were allocated from the river mouth to upper estuary *viz.* sampling Station 1 (Lat. 11°30.135' N; Long. 79°46.556' E), Station 2 (Lat. 11°29.051' N; Long. 79°45.577' E), Station 3 (Lat. 11°28.239' N; Long. 79°44.326' E), Station 4 (Lat. 11°27.641' N; Long. 79°43.699' E) and station 5 (Lat. 11°27.381' N; Long. 79°42.486' E) as indicated in Figure 1.

Surface water samples were taken at monthly intervals in the Vellar estuary using a Niskin water sampler for the analysis of nutrients, chlorophyll, and total alkalinity from May 2013 to December 2019. Among the five stations, the station 1 and 2 are considered as the lower estuary, station 3 as mid estuary and station 4 and 5 as upper estuary. Rainfall in the Vellar estuary ranged from 60 to 150 cm, with 70 – 80 % of the precipitation falling during the northeast monsoon (October to December) season[16]. Thus, the full data set was divided into four seasons: post-monsoon (January to March), summer (April to June), pre-monsoon (southwest monsoon - July to September), and monsoon (October to December) depending on the prevalence of northeast monsoon.

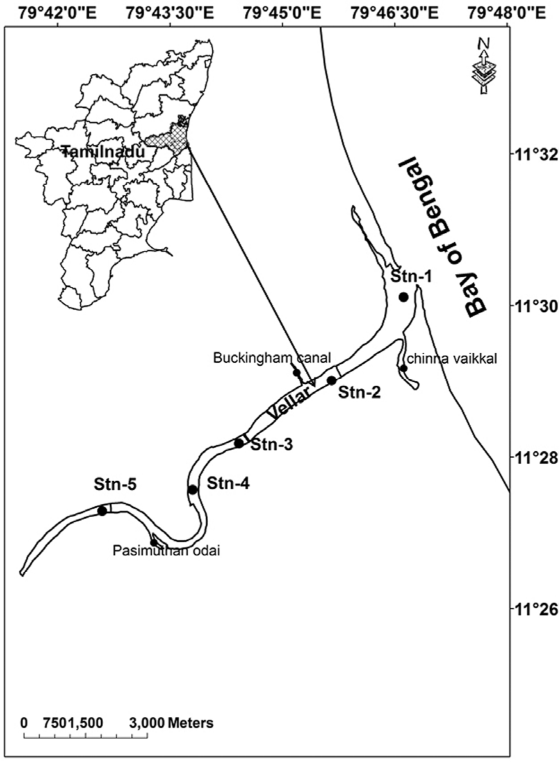

Fig. 1 — Map showing the study area

Estimation of environmental variables

A digital multi-stem thermometer with a ±0.1 °C precision was used to monitor Atmospheric Temperature (AT) and Surface Water Temperature (SWT). Salinity was measured with a handheld refractometer (Atago hand refractometer, Japan). The 905 Titrando sensor (Metrohm) was used to determine the Dissolved Oxygen (DO) using the modified Winkler's method[17]. Macronutrients dissolved in seawater such as nitrite, nitrate, ammonia, reactive silicate, and inorganic phosphate were estimated using a Shimadzu-UV 2450 UV-VIS spectrophotometer after filtering the water samples *via* a 47 mm GF/C filter paper with a millipore filtering system as described by Strickland & Parsons[17]. Particulate organic carbon was estimated using methodology given by Parsons *et al.*[18]. According to UNESCO[19], chlorophyll-*a* concentration was determined using a spectrophotometer (Shimadzu-UV 2450) calibrated with a chlorophyll-*a* standard (Sigma – C6144) and 90 % acetone.

Estimation of carbonate variables

Water samples were taken directly from the Niskin water sampler into a 250 ml polyethylene container for the measurement of carbonate variables, using clean drawing tubes with no air bubbles to avoid contamination from the atmosphere. pH was measured at *in-situ* temperature using a pre-calibrated pH meter (EUTECH – Cyberscan pH1100) (PH: 4.01, 7.00, 10.01, USA buffer option) at seawater scale with an accuracy of ±0.002. The Gran titration method[20] was used to assess the Total Alkalinity (TA) with a precision of ±2 μmol Kg^{-1} using 905 Titrando total alkalinity meter (Metrohm). CO_2Sys.v2.1 was used to calculate Dissolved Inorganic Carbon (DIC) and pCO_2 from measured SST, salinity, pH, and TA[21].

Air-water CO_2 flux

The air-water flux of CO_2 (FCO_2) was derived using Wanninkhof[22] and Weiss[23] methods, as outlined by Shanthi *et al.*[24].

Arithmetical analysis

The relationship between the environmental factors and pCO_2 was investigated using Multiple Llinear Regression (MLR) and Principal Component Analysis (PCA) in the statistical software SPSS V.16.0. One of the most successful methods for lowering the dimensionality of large datasets without compromising information is PCA analysis[25]. To achieve enhanced primary components of environmental importance[26], the varimax rotation was used. The factor loadings were calculated using eigenvalues greater than 1.5 and were grouped by absolute loading values greater than 0.5. Multiple regression analysis was used to evaluate the values of a dependent variable in respect to a set of predicted factors in order to determine the contribution of each variable to the pCO_2(ref 27).

Results and Discussion

Estuaries are considered as nutrient sinks or traps, where nutrient dynamics are unpredictable and significant which makes it a highly productive ecosystem[28]. Despite the proven evidences that the estuaries act as a CO_2 source to the atmosphere, the quantity, seasonality and the parameters influencing the changes differs each other depending on the factors indicated above. This becomes important for India as the estuaries of east and the west coast differs each other by the geomorphology, monsoonal regime, river water influx and tidal range.

Seasonal difference in environmental variables

Environmental variables such as chlorophyll and Particulate Organic Carbon (POC) showed clear temporal difference in the Vellar estuary between May 2013 and December 2019. The Atmospheric Temperature (AT) was observed to be high in the summer (32.8 °C) and low in the monsoon with 24.1 °C (Fig. 2). SWT found cold (24.0 °C) during monsoon coinciding with low AT (24.1 °C) whereas warm SWT (31.2 °C) during the summer, correlating with the maximum AT (32.8 °C) (Fig. 2). The increasing SWT was attributed to the increase in solar radiation available at the surface water, besides other influences such as evaporation, freshwater intake, chill and mixing and flow from the adjacent neritic waters[29]. The wind speed and seasonal rainfall may also be linked to the seasonal variations in SWT[30].

The low salinity (4 psu) was observed at upper estuary during the monsoon season which ensures the freshwater discharges into the estuary through seasonal rainfall and the high salinity (35 psu) registered in summer indicates the influence of neritic water without any riverine inputs (Fig. 2). The wide range of salinity (1 – 34 psu) recorded during monsoon indicates a brief period of fresh water discharge into the estuarine system through rainfall. During the peak flow period, the estuary's entire water column was of fresh water. Saline water gradually intruded into the estuary as the river discharge declined from moderate to insignificant.

The lowest measured level of DO (4.17 mg l^{-1}) during the post-monsoon season might be attributed to a lack of external inputs and subsequent degradation of organic materials derived through the riverine inputs which started to settled in the river beds in due course of time (Fig. 3). However, DO concentration was found high (7.69 mg l^{-1}) at lower estuary during monsoon that could be attributed to the wind forcing on the water masses, resulting in dissolution of atmospheric oxygen and the increasing rate of photosynthesis through phytoplankton production during the same period. On the contrary, DO in most of the estuaries is found to be below saturation level during monsoon period indicating the utilization of O_2 by heterotrophs during monsoon period[31]. Though high chlorophyll concentration (29.94 µg l^{-1}) was found during monsoon, increased heterotrophy observed during peak discharge period exceeds the biological production rate; hence it leads to the moderate DO concentration (Fig. 3).

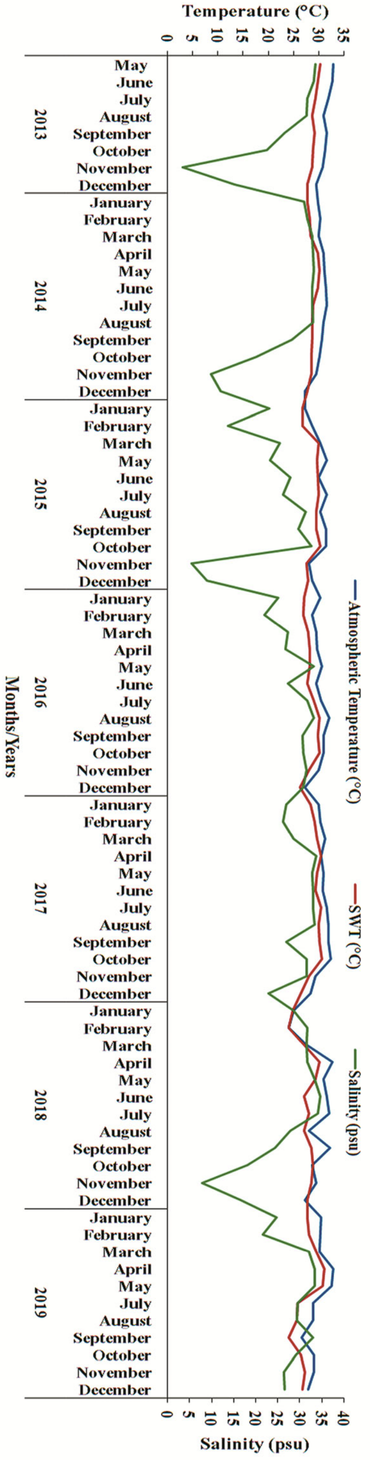

Fig. 2 — Inter-annual variation of atmospheric temperature, SWT and salinity in the Vellar estuary

The nutrients in the Vellar estuary shows clear seasonal pattern (nitrite: 0.14– 9.46 µM, nitrate: 0.78 – 20.99 µM, ammonia: 0.24 – 2.66 µM, IP: 0.18 – 10.58 µM, and silicate: 8.50 – 60.06 µM), chlorophyll

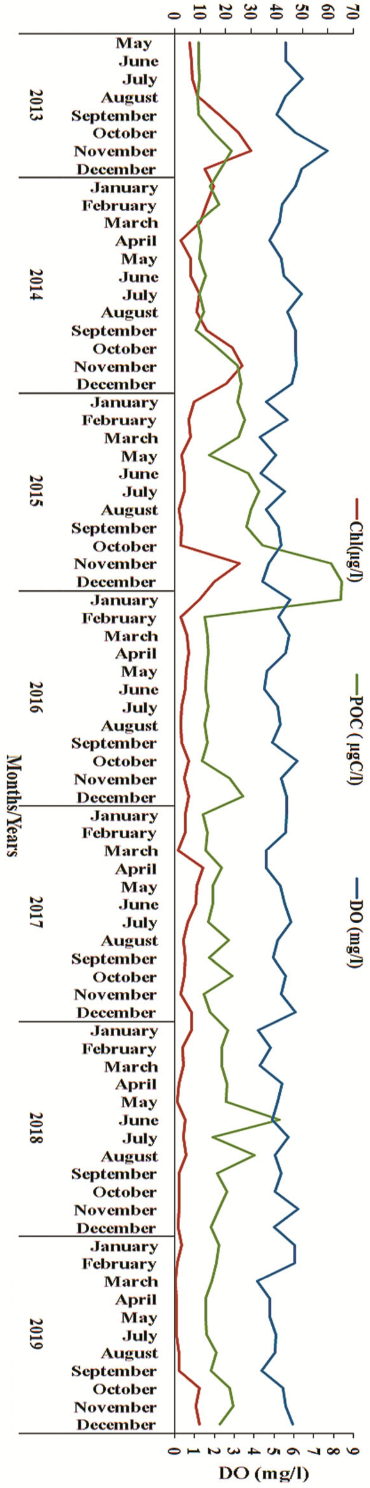

Fig. 3 — Inter-annual variation of chlorophyll, POC and DO in the Vellar estuary

(0.38 – 29.94 µg l^{-1}) and POC (8.27 – 65.59 µg C l^{-1}) registering the maximum concentrations during the monsoon as a result of terrestrial discharge, which carries nutrient loaded freshwater into the estuary as well as a high POC load derived from the terrigenous materials (Figs. 3 – 5). Rivers, ground water, atmosphere, land runoff and sediments[32] are primary sources of nutrients in shallow coastal habitats. Moreover, nutrient loads from river runoff vary greatly depending on the basin's[33] precipitation. According to Gupta *et al.*[34], Particulate Organic Matter (POM) is generally fresh and autochthonous throughout the summer, but it is primarily deteriorated and allochthonous during the monsoon season. During the monsoon season, the maximum chlorophyll concentration (29.94 µg l^{-1}) was observed at the lower estuary might be due to the freshwater derived blue-greens which flourished under the highest nutrient concentrations. While, upper estuary was found to be rich in suspended solids and organic matter load derived from the terrestrial inputs resulting in the decrease in biological production.

Seasonal difference in carbonate variables

During the study period, the Vellar estuary showed significant temporal fluctuation in carbonate variables (Fig. 6). The TA (1985 µM kg^{-1}) and DIC (1821 µM kg^{-1}) concentrations were low during the pre-monsoon of the year 2013 due to lack of external inputs and increased rate of photosynthesis. Significant biological production devours a considerable quantity of DIC and reduces pCO_2 (322 µatm, resulting in decreased DIC and pCO_2 in the surface water[35]. In addition, the ammonia arrived from bottom to the surface through wind driven vertical mixing has been utilized as a nutrient source during photosynthesis resulting in decrease in TA. While, the highest TA (6812 µM kg^{-1}) and DIC (6997 µM kg^{-1}) were observed in the 2015 monsoon season owing to land run-off, which carries weathered materials from rock and land derived DIC into the upper estuary. The increased load of nitrogenous nutrients in the estuary during this time also plays a significant role in determining the TA concentration as the ammonia inputs tend to decrease the TA by nitrification processes, while nitrate inputs increase the TA by denitrification process[36]. However, in the present study both ammonia and nitrate recorded maximum during monsoon period but the higher nitrate concentration over ammonia by 2 – 3 fold favours the

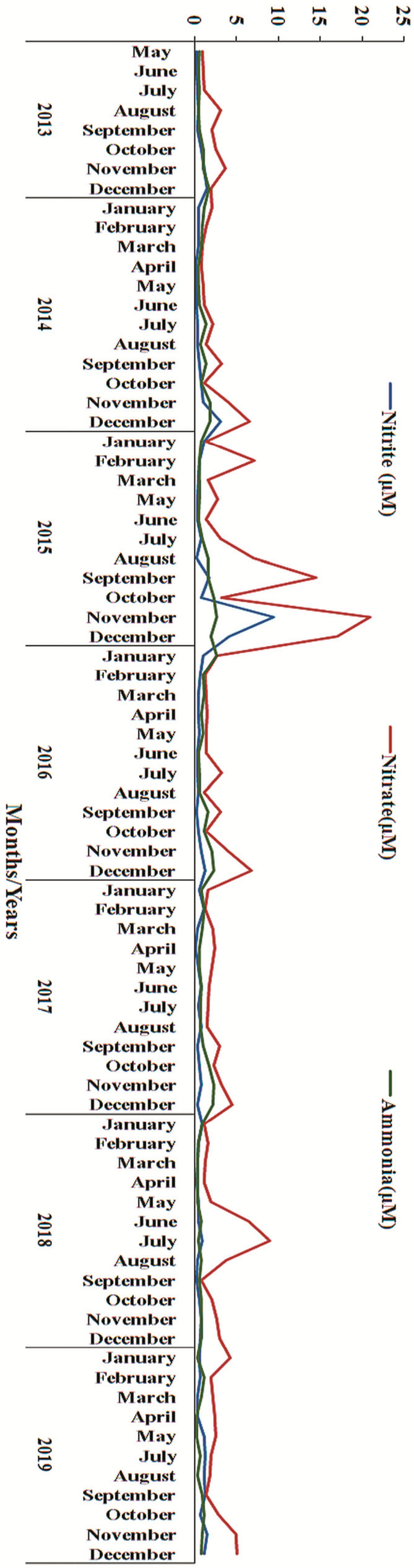

Fig. 4 — Inter-annual variation of nitrogenous nutrients in the Vellar estuary

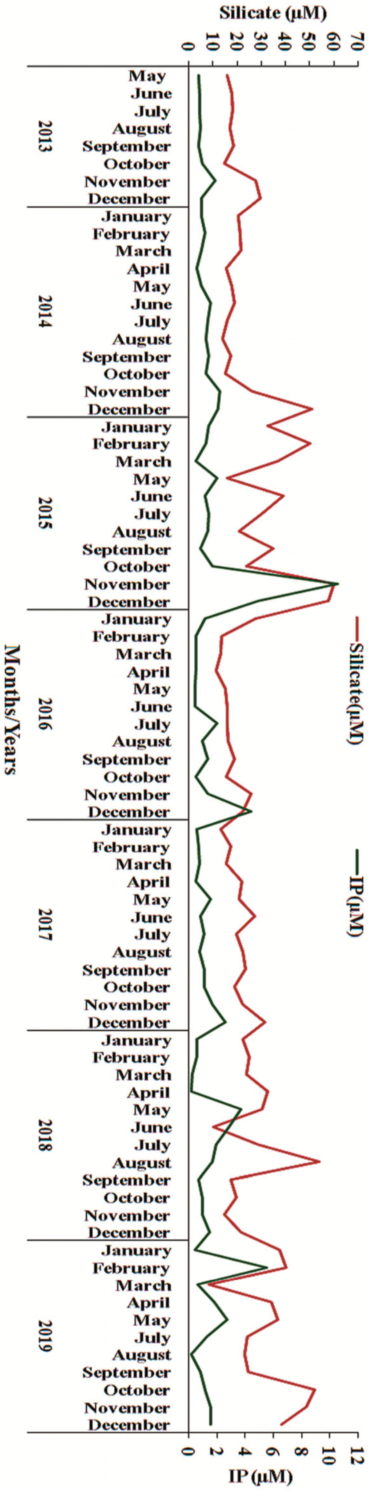

Fig. 5 — Inter-annual variation of silicate and IP in the Vellar estuary

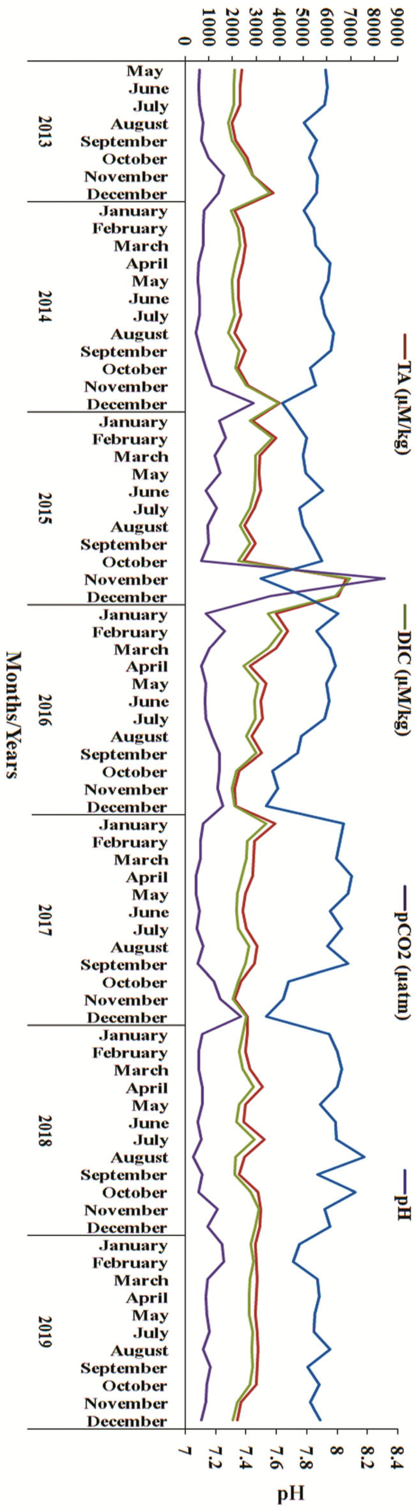

Fig. 6 — Inter-annual variation of carbonate variables in the Vellar estuary

denitrification process within the estuary thereby increasing the TA.

The lowest pH (7.498) was observed during the monsoon season in 2015 at upper estuary associated with high $p\text{CO}_2$ (8457 µatm). Over time, organic matter brought by river run-off deteriorates in the upper estuary, releasing CO_2 into the water column, leading to increased $p\mathrm{CO_2}$ level[37] and decreased pH. Such high $p\mathrm{CO_2}$ levels during discharge period were also seen in several other Indian estuaries, including, Chilka estuary[14], Mandovi-Zuari estuary[6], Cochin estuary[13] and Godavari estuary[12]. Being the shallow estuary, it remains turbid in most part of the year and it increases with increase in river flow influenced by rain runoff making the water column more turbid during monsoon. The turbidity inhibits the availability of light for biological production leading to weak biological draw down of CO_2. Further the small riverlets like Chinnavaikkal, Buckingham channel and Pasimuthan odai confluencing the estuary bring higher $p\mathrm{CO_2}$ from the mangrove and terrestrial vegetations; raising the $p\mathrm{CO_2}$ level in the estuary and emitting CO_2 into the atmosphere. The waters from mangroves on the lower estuarine bank function as a source of CO_2 to the atmosphere owing to heterotrophic nature of the water column and inter-tidal sediments[7]. CO_2-rich pore-waters inflow during ebbing in the estuary also contributes to the emission of CO_2 from the mangrove surrounding waters[37].

The maximum pH (8.182) with minimum $p\mathrm{CO_2}$ (322 µatm) was observed at the lower estuary during pre-monsoon in 2018 where the estuarine water mixes with the alkaline seawater due to strong southwest monsoon winds resulting decreases in the hydrogen ion concentration. Since, the maximum discharge of Vellar river is happening during monsoon season, the estuary is influenced only by neritic water during summer with higher salinity (35 psu). Comparatively, higher solar radiation and less turbidity during the summer increases the biological production resulting in reduced $p\mathrm{CO_2}$ during this season at the estuary. Moreover, the external inputs from the rivulets is also nil during this period as the low tidal range of less than 1 m is not good enough to wash the DIC from the adjacent mangrove and terrestrial vegetations.

Air – water CO_2 flux

The air-water CO_2 exchange has been calculated using the difference in $p\mathrm{CO_2}$ between the atmosphere and water. Air-water interaction on the water surface plays a significant role in determining the exchange. Seasonal variations in gas exchange are frequently connected with $p\mathrm{CO_2}$ distributions, which are typically highest at low salinities during the monsoon months. Because lower stations have larger surface areas and lower $p\mathrm{CO_2}$ values, the lower estuary flux was significantly lower than the upper estuary flux.

Air-sea CO_2 flux varied between -1.70 and 31.42 mmol C m^{-2} d^{-1} with the minimum during summer in 2016 and maximum during the monsoon season in 2014 (Fig. 7). The mean CO_2 outflows to the atmosphere over the four seasons were 2.05±1.58 mmol C m^{-2} d^{-1} for post-monsoon, 1.90±0.93 mmol C m^{-2} d^{-1} for summer, 4.86±4.66 mmol C m^{-2} d^{-1} for pre-monsoon and 8.61±5.06 mmol C m^{-2} d^{-1} for monsoon. The atmospheric $p\mathrm{CO_2}$ level varied from 353 to 405 µatm in the corresponding period with the highest levels during post-monsoon and summer and the lowest levels during the pre-monsoon season. Flux discrepancies across the seasons are due to decreased wind forcing despite high $p\mathrm{CO_2}$ levels[6]. Increased biological synthesis of organic matter will start withdrawing surface water DIC and $p\mathrm{CO_2}$, favouring an increase in atmospheric CO_2 absorption during the pre-monsoon, which will offset the impacts of increased production[38].

The mean flux of the Vellar estuary amounts to 4.13±5.59 mmol C m^{-2} d^{-1} which is in order of scale lower than that of major Indian estuaries, such as 21.9±26.1 mmol C m^{-2} d^{-1} in Godavari estuary[12], 267±131 mmol C m^{-2} d^{-1} in Cochin estuary[13] and 14.4 mmol C m^{-2} d^{-1} in Chilka lake[14]. On the whole, the Vellar estuary exhibited the average $p\mathrm{CO_2}$ of 1068 µatm and supersaturation with regard to atmospheric $p\mathrm{CO_2}$ all over the year. Overall, the Vellar estuary was significant source of carbon (355.48 mol C m^{-2} Y^{-1}) to the atmosphere in the period of study.

Arithmetical analysis

Principal Component Analysis (PCA)

PCA extracted four Principal Components (PC) constituting 77.28 % of cumulative variance (Table 1). PC1 covers 37.27 % of the total variance with positive loading of TA, DIC, $p\mathrm{CO_2}$, nitrite, nitrate, IP, silicate and POC and negative loading of salinity which clearly indicates that the water having highest salinity are devoid of nutrients, TA, DIC and $p\mathrm{CO_2}$ during no discharge periods. Whereas during the discharge period, the estuarine water was enriched with nutrients, TA, DIC and $p\mathrm{CO_2}$ because of the terrestrial inputs from the freshwater runoff. The soil is the predominant source of organic carbon during the monsoon season, whereas phytoplankton production is the primary source during the summer and pre-monsoon seasons[39]. Balakrishna & Probst[39] also reported that during the monsoon season, 3 – 91

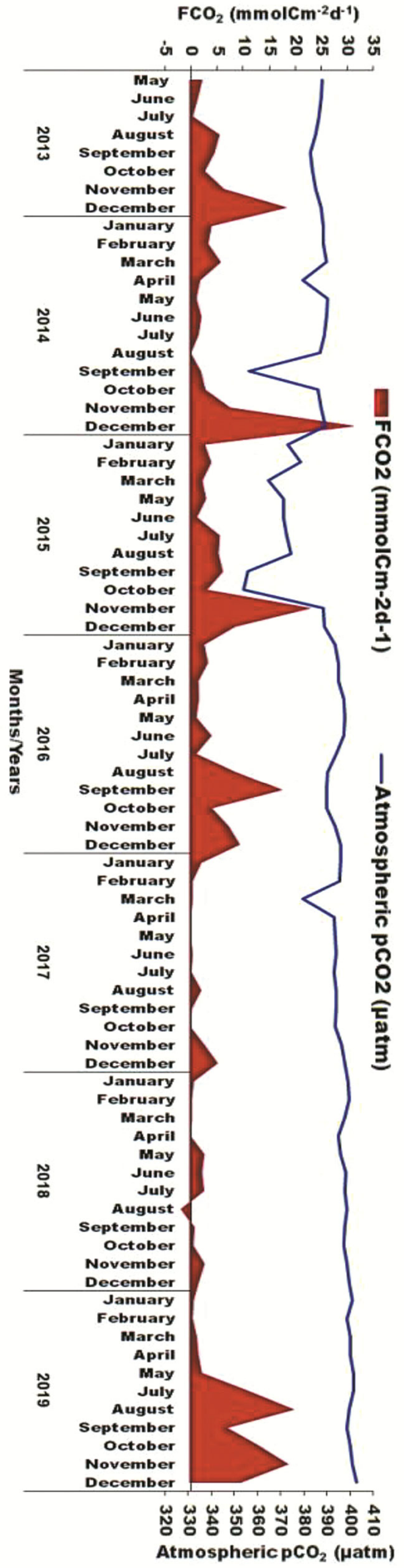

Fig. 7 — Inter-annual variation of air-sea CO_2 flux and atmospheric $p$$CO_2$ in the Vellar estuary

Table 1 — Factor loadings of physico-chemical and carbonate variables in the Vellar estuary

	Components			
	1	2	3	4
AT	-.179	-.063	0.95	.017
SWT	-.076	-.080	0.94	-.021
DO	-0.58	-.002	.233	-0.64
Salinity	-.266	.167	.140	0.83
pH	-.132	-0.85	.053	-.095
TA	0.94	-.076	-.071	.019
DIC	0.94	.015	-.099	.075
pCO2	0.79	0.48	-.067	.163
Nitrite	0.83	.362	-.113	.156
Nitrate	0.76	.406	-.012	.036
Ammonia	.284	0.7	-.126	.203
IP	0.66	0.53	.034	.062
Silicate	0.61	.193	-.227	.035
Chlorophyll	.247	.143	-.044	0.8
POC	0.72	.241	-.125	-.003
Eigen values	5.591	2.188	1.969	1.844
% of variance	37.270	14.585	13.128	12.295
Cumulative %	37.270	51.855	64.983	77.278

times more organic carbon is delivered to the ocean than in the summer, which might sustain heterotrophic activity. During the rainy season, Sarma *et al.*[6] reported $p$$CO_2$ values of > 2000 µatm in the Mandovi-Zuari estuarine system of Goa that agrees with the findings of net heterotrophy by Ram *et al.*[40]. As a result, increased bacterial respiratory activity might possibly elevate the $p$$CO_2$ levels in the Vellar estuarine system during the monsoonal discharge.

PC2 accounted for 14.58 % of the variability when $p$$CO_2$, IP, and ammonia were all positive and pH was negative suggesting the occurrence of highest $p$$CO_2$ and FCO_2 in lowest pH freshwater enriched with terrestrial derived nutrients and organic carbon load during rainy season. PC3 described the positive AT and SWT loading with a total variance of 13.13 %, demonstrating the effect of light intensity in both AT and SWT throughout the year. Moreover, temperature is critical to the inorganic carbon system's thermodynamic equilibrium and to the net ecosystem metabolism inside the estuary. With a total variance of 12.29 %, PC4 reflects the negative loading of salinity with the positive loading of DO and chlorophyll, confirming that biological production plays a significant role in DO dispersion in the water column.

Multiple linear regression analysis

A substantial relationship between hydro-biological factors and $p$$CO_2$ was found using multiple linear regressions modelling and yielded the following equation:

pCO_2 = 2958.370 – 26.425*AT +66.084*SWT – 0.366*DO +15.837*Salinity – 563.120*pH – 2.946*TA + 3.475*DIC + 332.356*nitrite + 7.289*nitrate – 7.983*ammonia + 105.245*IP + 1.260*SiO_3 + 1.161*Chlorophyll – 5.395*POC

The results of multiple regression summary (R^2 = 0.957, SEE±230.82, $p < 0.001$, N = 230) explained positive influence of SWT, DO, salinity, DIC, nitrite, nitrate, IP, silicate and chlorophyll and negative influence of AT, pH, TA, ammonia and POC on the pCO_2 distribution. Thermodynamically, pCO_2 increases at a rate of roughly 4 % $°C^{-1}$ as temperature rises[41]. The positive relationship obtained between SWT and pCO_2 pointed that SWT had a significant impact on CO_2 solubility in the water column and its seasonal variation in the estuary. The negative association between pH and pCO_2 indicates that extensive organic matter degradation in the estuary is driving a fall in pH and enhances the pCO_2 levels[9]. Similarly, the negative relationship of ammonia with pCO_2 was mainly because of the heterotrophic metabolism which mineralizes a major portion of the organic carbon transported by the riverine inputs[42]. Through the nitrification process, nitrate concentration increases among the nitrogenous nutrients as well as nitrification lowers the total alkalinity[36], which is evident from the positive relationship of nitrate and negative relationship of TA with pCO_2. Furthermore, the nitrification process causes the estuary water to become acidic, which promotes CO_2 release to the atmosphere[43]. The depletion of oxygen caused by organic matter remineralization is accompanied by a rise in DIC, TA, and pCO_2 as well as a reduction in pH in the inner and upper estuaries.

Borges[44] revealed high pCO_2 values in various estuaries and rivers with net heterotrophy which was supported by terrestrial organic carbon. Similar phenomenon was described in the Cochin Estuary[45]. Despite other estuaries in India, the Godavari estuary has a perennial incidence of heterotrophy, including bloom seasons[33]. The quantification of nutrient transport from estuary to ocean is critical because it may boost primary production and reduce surface pCO_2 in the coastal Bay of Bengal.

Conclusion

The Vellar estuary's seasonal cycle revealed a trend of reduced nutrients and pCO_2 from post-monsoon to pre-monsoon followed by increased pCO_2 levels and nutrients during the monsoon season. Except during the summer months, the Vellar estuary was a net CO_2 provider to the atmosphere, with increasing monthly CO_2 fluxes from the estuary. The positive relationship of SST and atmospheric temperature with pCO_2 in multiple linear regression analysis depicted that temperature fluctuations accounted for a greater proportion of the pCO_2 variability. Aside from that, biological processes were proven to be important which is evident from the positive influence of chlorophyll, POC, nitrite, nitrate and silicate on pCO_2 distribution. During monsoon season, storm events and subsequent rainfall brought large amount of freshwater discharge which is rich in organic carbon load leading to the production of elevated pCO_2 levels. On an annual basis, river discharges also have a significant effect on CO_2 exchange from the estuary. When compared to the other Indian estuaries, the Vellar estuary's contribution to CO_2 flux to the atmosphere was found minimal. The amount of organic carbon and nutrients exported determines whether the neighbouring coastal region is a net sink or generator of CO_2 to the atmosphere, and hence the influence of Vellar estuary discharges on the coastal Bay of Bengal. During the monsoon, most of the Indian estuarine systems become heterotrophic, with land-derived organic materials predominantly fueling the bacterial activity. Time-series studies in the current investigation revealed that terrestrial organic carbon associated with Vellar River freshwater discharges plays a vital role in the estuarine ecosystem's metabolic balance, making the estuary a substantial source of CO_2.

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Conflict of Interest

Authors declare no opposing or conflict of interest.

Author Contributions

RS – Analysis, investigation, draft writing; DP - Formal analysis, exploration; AS – Supervision; TT –

Conceptualization, evaluation & editing, resources; and SBC & RR – Funding acquisition.

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