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Research Article

Intra-annual Variability of CO2 Flux in the Mahanadi Estuary- A Tropical Estuarine System, India

Abstract

The inorganic carbon dynamics and the CO_2 flux of estuarine system are strongly influenced by the productivity and nutrient regime of water. This study provides full seasonal coverage of assessment of the physicochemical variables of Mahanadi estuary, mainly focusing on the carbonate system through the measurement of pH, Total Alkalinity (TA), Dissolved Inorganic Carbon (DIC), both aqueous and air fCO_2, Dissolved Oxygen (DO) and chlorophyll *a* (chl *a*). The relationship of TA and DIC were found conservative throughout the study period. The estuary was found to be over-saturated with CO_2 and acted as a net source. However, the magnitude of flux varied from season to season with a range between -8.14 to 58.09 μmol m^{-2} h^{-1} indicating ephemeral sink phase in the estuary. The air-water CO_2 flux was primarily governed by fCO_2 (water) although other factors such as temperature, pH, salinity, total alkalinity, wind speed and fCO_2 (air) noticeably affected CO_2 flux. A strong positive correlation was observed between temperature and inorganic nutrients during the study period. The study of net ecosystem metabolism justifies the heterotrophic nature of Mahanadi estuarine system.

Abbreviations

Chl a: Chlorophyll a; DIC: Dissolved Inorganic Carbon; DIN: Dissolved Inorganic Nutrients; DIP: Dissolved Inorganic Phosphates; fCO_2(Air): Fugacity of CO_2 in Air; fCO_2(Water): Fugacity of CO_2 in Water;

Introduction

The magnitude of flux determines the nature of an oceanic system to act as a net sink or source of atmospheric CO_2 with the simultaneous activity of production and respiration [1,2]. The uncertainty in flux estimation results in complication in characterising an oceanic system [3,4]. Changes in land use and vegetation cover affect the carbon stocks which are responsible for the inter-conversion of a productive system to a heterotrophic one and vice versa [5-8]. The sink potential of an ecosystem is characterised by the solubility pump and the biological pump of CO_2. The physical variables that are responsible for altering the solubility pump are temperature, salinity and wind velocity. The dissociation of carbonic acid to carbonate and bicarbonate is also a governing factor for solubility pump. On the other hand, the production of plant materials by autotrophic activities is related to the biological pump. Production of calcifying phytoplankton drive the calcium carbonate pump by releasing CO_2 while the non-calcifying phytoplankton contributes to the organic carbon pump by absorbing CO_2 in the uppermost layer of the ocean [9]. Part of the organic carbon is used and recycled in the upper surface layer through microbial processes and rest sinks down to the bottom and continues to decompose due to bacterial respiration. The intense anthropogenic perturbation in the coastal ocean alters the biological pump as well as the solubility pump and cause variation in the source-sink strength [10]. The nutrient upwelling significantly affects the biological pump causing phytoplankton bloom, while river run-off causes dilution and changes the solubility pump [11]. Hence, coastal ocean is a very dynamic system having variable source-sink strength due to the temporal and spatial variation in the input of terrestrial organic matter (makes the system heterotrophic) and nutrients (makes the system autotrophic) [12,13].

In general, the open ocean acts as a net sink for atmospheric CO_2 with a magnitude ranging between -1.4 PgC yr^{-1} and -2.2 PgC yr^{-1} [14]. However, the role of the coastal ocean in global CO_2 budget remains speculative due to the paucity of data [15,16]. The absorption of CO_2 from continental shelves by the global extrapolation of air-water CO_2 flux values or by compiling the data set of different continental shelves available in the literature is between -0.22 PgC yr^{-1} to -1.0 PgC yr^{-1} [15,17,18]. The global emission of CO_2 by estuaries to the atmosphere is 0.27 PgC yr^{-1} [16]. Frankignoulle et al. [6], showed that the CO_2

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emission was between 0.03–0.06 Pg C yr^{-1} which represents 5 to 10% of anthropogenic CO_2 emission for Western Europe.

Estuaries in India are driven by monsoonal rainfall. Hence, the biogeochemical cycling of materials during discharge period is far different from the dry period [19]. During peak discharge period, the estuary assumed riverine condition while in other seasons, the estuary is expected to be dominated by seawater influence [20-22]. Hence, the objective of this study was to determine the seasonal behaviour of CO_2 absorption/emission in the Mahanadi estuarine region and to characterise the biogeochemical processes that prevail the estuarine system.

Materials and Methods

Geographical settings of study area

The Mahanadi river system is the third largest in the Indian peninsula and the largest river system in the state of Odisha, The basin (19°20'to 23°35'N and 80°30'-86°50'E) has a total length of 851 km, extending over an area of ca 141,600 km^2 (65628 km^2 in Odisha) and a pick discharge of 44,740 $m^3 s^{-1}$ [23]. The river begins in the Baster plateau in Raipur district of Chhattisgarh, flowing over different geographical formations of Eastern Ghats and joins the Bay of Bengal after divided into a network of branches in the deltaic area. The main branch of Mahanadi River meets the Bay of Bengal at Paradip. From the environmental features and topographic point of view, the estuarine system of Mahanadi River has been ranked as a tide-dominated coastal plain and the tidal estuarine part of the river covers a length of 40 km and has a basin area of 9 km^2 [23].

Anthropogenic influence

The River Mahanadi receives water from the industrial cities of Sambalpur, Cuttack, Bauda, Choudwar, Jagatpur and Paradip. It also receives effluents from some industries like fertiliser, paper textiles, and agriculture run-off along its course from various cities [24,25]. The major anthropogenic influence has been ascribed by mainly three populated urban settlements on the banks of the river, namely Cuttack, Sambalpur and the port city Paradip due to the propagation of industries. The river contributes as a significant source of Domestic water supply to many cities on its bank and consequently it receives back the untreated domestic water and industrial effluents from different industries situated near side to the river.

Sampling strategy

Indian Meteorological Department (IMD) designates four climatological seasons such as winter (December - March), summer or pre-monsoon (April - July), Monsoon or rainy (July - September) and post-monsoon or autumn (October - November). Accordingly, the sampling was carried out at 11 different stations in the Mahanadi estuary twice during each season following the IMD seasonal pattern. The surface samples (few centimeters below the sea surface) were collected by hiring trawlers.

Analytical protocol

Salinity, pH and temperature were immediately measured on site by using WTW kit (WTW model multi 340) fitted with Sentix 41 probe for pH and Tetracon 325 probe for temperature and salinity. Before each sampling, the pH electrode was calibrated with the standard pH buffers (WTW Technical Buffer Model TEP Trace) having pH at 4.01, 7.00 and 10.01. The water samples for DO analysis were collected in the glass stopper bottles. The samples were immediately fixed and then determined by Winkler's method modified by Grasshoff [26]. Gross primary productivity (GPP) and community respiration (CR) were measured following the DO method of APHA [27] using *in situ* light and dark bottles incubation. The dark bottles were wrapped with black tape and aluminium foil. The dissolved oxygen in both light and dark incubated samples was fixed immediately upon retrieval. The changes in DO concentrations in light bottles between initial and after incubation were used as a measure of Net Primary Production (NPP). Changes in DO in dark bottles were used to quantify CR. GPP was estimated as the sum of NCP and CR. The metabolic rates measured using changes in DO concentrations were converted to carbon units assuming a photosynthetic quotient 1.25. The water samples were preserved and analyzed as per standard methods [27]. Dissolved inorganic nutrients (nitrate, nitrite, ammonia, silicate, and phosphate) were determined by standard spectrophotometric methods [28] using Varian 50 bio UV-visible spectrophotometer. TA and pH (for concurrence and these values have been presented in the text) were determined by potentiometric (Metrohm 905 Titrando, Switzerland) Gran titration method. 40 mL of measured sample was titrated against an accurately standardized 0.1 N sulfuric acid. The sulfuric acid was standardized by analytical grade sodium carbonate (Merck). Total Organic Carbon (TOC) was estimated using Elementar-Vario-TOC analyzer. The analyser was standardised with potassium phthalate and sodium carbonate. The temperature of the combustion tube was maintained at 850 °C for the catalytic combustion of the water sample. The fCO_2 (water) and DIC were computed using measured salinity, temperature, pH, nutrients (phosphate and silicate) and alkalinity with the help of CO_2SYS.EXE software [29]. The dissociation constants K_1 and K_2 were used according to Peng et al. [30]. Apparent oxygen utilization (AOU) was calculated using the solubility equation of Benson and Krause [31]. The concentration of CO_2 (in parts per million) in the overlying atmosphere was determined by a non-dispersive infrared gas analyzer (Li-840A CO_2/H_2O gas analyzer, Li-COR Inc., USA), 10 m above the water surface water. The analyzer was calibrated with the help of three gases—one having CO_2-free air and the other two having a certified standard of high concentration of 300 and 600 ppm of CO_2, respectively (Indian Refrigeration Stores, Kolkata, West Bengal, India). The measured CO_2 in ppm was converted to fCO_2 (air) using the virial equation of state [32]. The wind speed data was obtained from the IMD.

The suspended particulate matter was measured by filtration methods implementing the gravimetric technique. Chl *a* of water samples were measured by filtering 1000 mL of water sample through Whatman GF/F (47mm diameter) using parallel filtration under low vacuum pressure. After filtration chl *a* was immediately extracted by immersing the filter paper in 10 mL of 90% acetone (Merck) and preserved at 4 °C for

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overnight extraction. The digest was centrifuged at 5000 rpm for 15 minutes and the absorbance of the supernatant was measured with a spectrophotometer [33] and the values were quantified using the equations of Jeffrey et al. [33].

Air-water CO_2 exchange

Flux densities (µmol m^{-2} h^{-1}) across the water–atmosphere were calculated according to the expression

$$fCO_2 = k.\beta.\Delta fCO_2 \quad (1)$$

where 'k' is the Gas Transfer Velocity (cm h^{-1}), 'β' is the Ostwald dilution Coefficient (mol m^{-3} atm^{-1}) and ΔfCO_2 is the difference in fugacity of CO_2 between water and air, [fCO_2 (water) - fCO_2 (air)]. Gas transfer velocity 'k' (cm h^{-1}) was calculated according to the equation [34]

$$k = 0.17\ u_{10} \left(\frac{660}{Sc}\right)^{2/3} for\ u_{10} \le 3.6\ ms^{-1} \quad (2)$$

$$k = (2.85u_{10} - 9.65)\left(\frac{660}{Sc}\right)^{0.5} for\ 3.6 \le u10 \le 13\ ms^{-1} \quad (3)$$

where u_{10} is vand the Schmidt number (Sc) for CO_2 was evaluated as per the formula,

$$Sc = A - Bt + Ct^2 - Dt^3 \quad (4)$$

where A = 1992.1, B = 121.86, C = 3.54, D = 0.04227 and t = Temperature (°C) of water [35]. The positive magnitude of fCO_2 interprets flux from water to air and vice versa.

Results and Discussion

Hydrodynamic characteristics

The surface temperature of Mahanadi estuary (Table 1) was found to be higher in monsoon (30.96 ± 0.32 °C) and lower in winter (24.4 ± 0.20 °C) and did not show any strong spatial variation throughout the study period. The distribution of pH was found to be higher in post-monsoon (8.07 ± 0.06) as the river was derived of run-off and lower in monsoon (7.84 ± 0.08). As expected low saline water was observed during monsoon (4.08 ± 0.34 psu) due to the fresh water supply to the estuary and higher during pre-monsoon (13.14 ± 4.44 psu). A load of suspended particulate matter was recorded high during monsoon (167 ± 73.7 mg $L^{-1)}$ and lower (7.04 ± 1.55 mg L^{-1}) during post-monsoon. Dissolved oxygen concentration was found to be higher during post-monsoon (7.42 ± 0.46 mg L^{-1}) followed by low AOU (-16.34 ± 14.20 µmol kg^{-1}) and low during monsoon (6.16 ± 0.21 mg L^{-1}) followed by high AOU (14.25 ± 6.92 µmol kg^{-1}). There was a wide seasonal variability of dissolved inorganic nutrients among the seasons. The higher values of DIN and DIP were recorded in monsoon (15.86 ± 0.90 µmol L^{-1} and 5.92 ± 1.81 µmol L^{-1} of DIN and DIP, respectively) whereas the lower values were obtained during winter (3.47 ±0.85 µmol L^{-1} and 0.38 ± 0.16 µmol wL^{-1}). The concentration of chl *a* was found to be high in pre-monsoon (4.57±0.78 mg m^{-3}) and low in winter (1.76±0.52 mg m^{-3}).

CO_2 dynamics

Seasonal variation of carbon components in Mahanadi estuary is depicted in Table 2. The River Mahanadi discharges freshwater into the estuary during monsoon which is loaded with both allochathonous organic carbon and inorganic nutrients. However, the CO_2 concentration was supersaturated during monsoon (598 ±161 µatm). The fCO_2 (water) showed wide variation in Mahanadi estuary (Figure 1). It varied between 281-1244 µatm throughout the year. The low fCO_2 (water) value was observed during post-monsoon (469 ± 83 µatm) due to less input of terrestrial carbon. The fCO_2 (water) value observed was somehow close to the previous report (~615-1807 µatm) by Ganguly et al. [36]. However, the concentration of CO_2 in other Indian estuaries was found to vary widely: Godavari estuary- ~221-34026 µatm [37], Hooghly estuary- 234-518 µatm [38], Mandovi estuary- ~4993 [39], Zuari estuary- ~2076 µatm [39], Krishna estuary- ~7473 µatm [40], Cauvery estuary--2989 µatm [40]. The CO_2 level observed in Indian estuaries is governed by two biological phenomena such as heterotrophic respiration and autotrophic production. The dominance of one phenomenon over the other varies from the estuary to estuary. In Cochin estuary [41], Chillika estuary [41], Mandovi and Zuary estuaries [39], high level of CO_2 is associated with heterotrophic respiration than autotrophic production. In the Mahanadi estuary, the CO_2 level is dominated by autotrophic production throughout the year. However, the magnitude of production varies from season to seasons. In addition to this, the fCO_2 (water) showed a negative correlation with dissolved oxygen concentration (R^2-0.30) suggesting intense oxygen utilisation for decomposition of organic matter thereby decreasing pH. The highest average value of fCO_2 (air) was observed during pre-monsoon (408 ± 2.98 µatm) and the lowest average value was found to be 380 ± 2.97 µatm in monsoon. The Δ fCO_2 value ranged between -122-864 µatm throughout the year. As the variation of fCO_2 (air) was found to vary in a narrow range of

Table 1: Mean ± SD of different physicochemical parameters in Mahanadi estuary.

Parameters	Winter	Pre- Monsoon	Monsoon	Post- Monsoon
Temperature (°C)	24.4±0.20	27.93±0.74	30.96±0.32	28.64±0.41
pH	8.06±0.03	7.99±0.08	7.84±0.08	8.07±0.06
Salinity (PSU)	6.04±2.94	13.14±4.44	4.08±0.34	4.36±1.37
SPM (mg L^{-1})	12.7±1.33	11.6±2.68	167±73.7	7.04±1.55
DO (mg L^{-1})	7.36±0.23	6.65±0.83	6.16±0.21	7.42±0.46
AOU (µmol kg^{-1})	-0.84±7.38	-0.51±26.98	14.25±6.92	-16.34±14.20
DIN (µmol L^{-1})	3.47±0.85	5.36±1.27	15.86±0.90	6.14±2.18
DIP (µmol L^{-1})	0.38±0.16	5.30±2.68	5.92±1.81	5.89±2.19
Chl *a* (mg m^{-3})	1.76±0.52	4.57±0.78	4.04±0.80	3.83±0.62

Table 2: Seasonal variation of carbon components in Mahanadi estuary (Mean value with standard deviation).

Parameters	Winter	Pre- Monsoon	Monsoon	Post- Monsoon
TA (µmol kg^{-1})	1937±132	1774±100	1211±93	1729±40
TOC (mg L^{-1})	3.83±0.49	2.33±0.39	3.34±0.28	7.29±1.13
DIC (µmol kg^{-1})	1855±125	1661±109	1181±92	1645±45
fCO_2 (water) (µatm)	515±63	501±136	598±161	469±83
fCO_2 (air) (µatm)	389±8.06	406±2.98	380±2.97	398±4.41
FCO_2 (µmol m^{-2} h^{-1})	0.48±0.24	6.33±9.11	14.79±10.78	0.83±1.00

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376-411 µatm, therefore it can be stated that the Δ fCO_2 was mainly influenced by fCO_2 (water) (Figure 2). There was a conserved relationship between TA and DIC in the Mahanadi estuary throughout the study period. TA was found to vary between 1102-2206 µmol kg^{-1} during the observation period. However, TA and DIC were found maximum with an average value of 1937 ± 132 µmol kg^{-1} and 1855±125 µmol kg^{-1}, respectively during winter and minimum 1211 ± 93 µmol kg^{-1} and 1181±92 µmol kg^{-1}, respectively during monsoon. Concentration levels of these two parameters, observed in Mahanadi estuary during monsoon, were much lower as compared to the previous report by Sarma et al. [37], (1951± 132 µmol kg^{-1} and 1590 ± 40 µmol kg^{-1}, respectively). The difference may be attributed to the sampling sites of the two studies. The inner estuary is taken for the present study, while Sarma et al. [37], selected sampling sites in the offshore region. Further, a significant change in the catchments of the river system has also occurred during this period and this is expected to influence the TOC input into the estuary, thus altering the DIC. There was a significant strong positive correlation between TA and DIC (R^2-0.99). It may be noted that the DIC is dependent on carbonate alkalinity and the relationship in such case is more or less inverse. However, the direct relationship between DIC and TA in present case infers that the observed alkalinity in Mahanadi estuary is more of non-carbonate type.

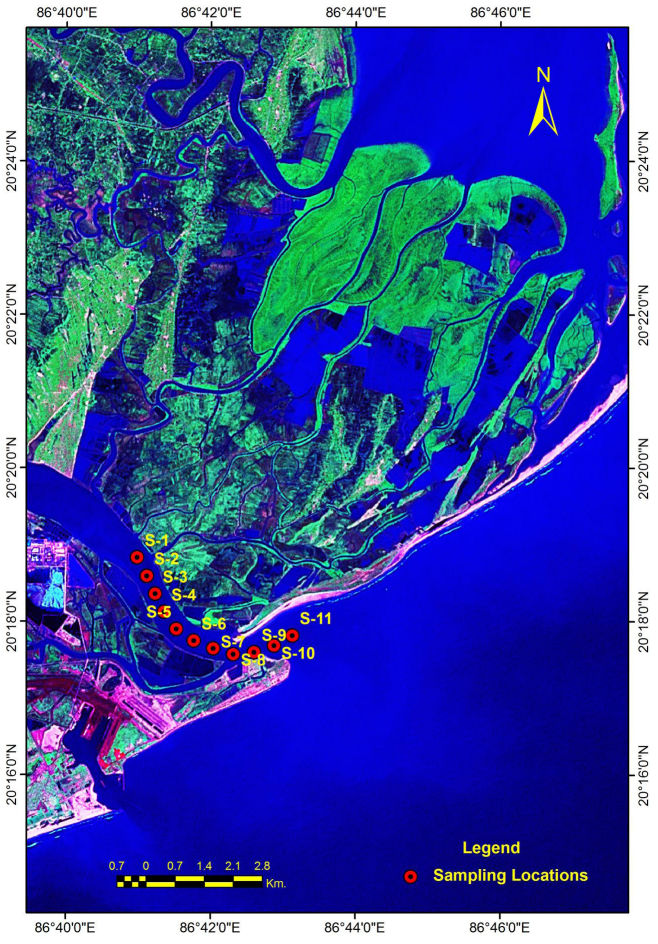

Figure 1: Study area showing the sampling locations of Mahanadi estuary.

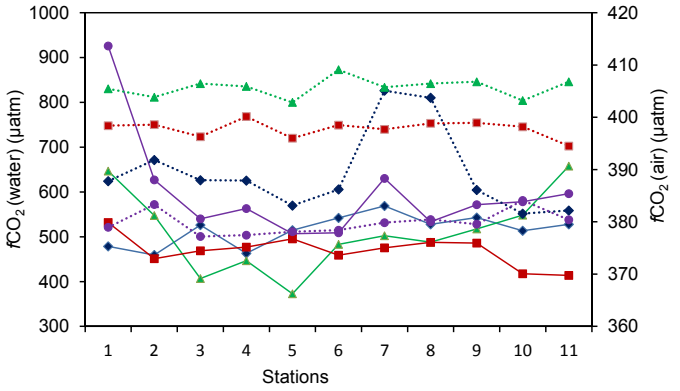

Figure 2: Seasonal variation of fCO2 (water) (solid line) and fCO2 (air)(dashed line) along 11 stations of Mahanadi estuary during 2014. Legends: - winter; -pre-monsoon; -monsoon; -post-monsoon

Effect of temperature and salinity

Surface water temperature of the estuary showed a significant negative correlation with the TA (R^2-0.71) while the temperature was significantly and positively correlated with DIN (R^2-0.64) and DIP (R^2-0.49). The mentioned relationship (Figure 3) may be attributed to the high bacterial activity that was observed at high temperature leading to increased rate of CO_2 release and organic matter oxidation. Consequently, the microbial metabolism at elevated temperature caused the release of nitrogen and phosphorous through degradation of organic substrates and resulted in a temperature triggered increase in DIN and DIP [42,43]. The TA of water showed a significant positive relationship with the salinity gradient of the estuary. Conversely, there was a decrease in FCO_2 and fCO_2 (water) in the same salinity range (Figure 4). While fCO_2 (water) was significantly correlated with salinity such correlation with fCO_2 was found insignificant. The increase in alkalinity *vis-a-vis* the decrease in fCO_2 (water) may be attributed to the reduced rate of autochthonous CO_2 production and resultant absorption of CO_2 from the air. The system was oriented towards carbonate production increasing the rate of CO_2 absorption at higher salinities.

Air-water CO_2 flux

The aquatic system can act as a significant source or sink on regional to global scale [44,45]. The inorganic nutrients and organic carbon before entering the ocean are processed in the estuary. Some parts of estuaries are autotrophic while others are heterotrophic which acts as strong exporters of CO_2 to the atmosphere [46,47]. The exchange of CO_2 between an aquatic system and the overlying atmosphere in an area of interest is governed by two decisive factors namely the concentration gradient between the water and the air and another is the turbulent energy in the surface aqueous boundary [48]. The methodology for measuring the CO_2 concentrations in both water and air in any aquatic regime has become simple and accurate [49,50]. There are various measuring procedures and equations for the determination of gas transfer velocity. Computation of gas transfer velocity using floating dome and gas tracers are problematic to handle and also overestimate the

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fluxes [51]. However, the predictive equations and gas tracer experiments are quite useful to suggest that at average wind speeds, tidal velocities, and estuarine depth, the gas transfer velocity appears in the range of 3-7 cm h^{-1} [51]. The CO_2 flux calculation exhibited that the Mahanadi estuary acted as a source throughout the year. The CO_2 efflux from water to air was observed maximum in the monsoon with an average value of 14.79 ± 10.78 µmol m^{-2} h^{-1} and minimum in winter (0.48 ± 0.24 µmol m^{-2} h^{-1}). This is in concurrence with the expected organic carbon input into the estuary from the terrestrial catchments and their degradation in the estuary. In pre-monsoon, a lesser magnitude of flux was found (6.33±9.11 µmol m^{-2} h^{-1}) as compared to monsoon. However, the flux value varied between -8.14 to 58.10 µmol m^{-2} h^{-1} throughout the year. Out of 88 observations, nine only showed negative flux values, which were attributed to post-monsoon period suggesting some areas of the estuary (towards the estuarine end) acted as a sink for cooler months. This indicated that though there was an ephemeric phase of net autotrophy, there was prolonged and dominant phase of heterotrophy in the estuary making it

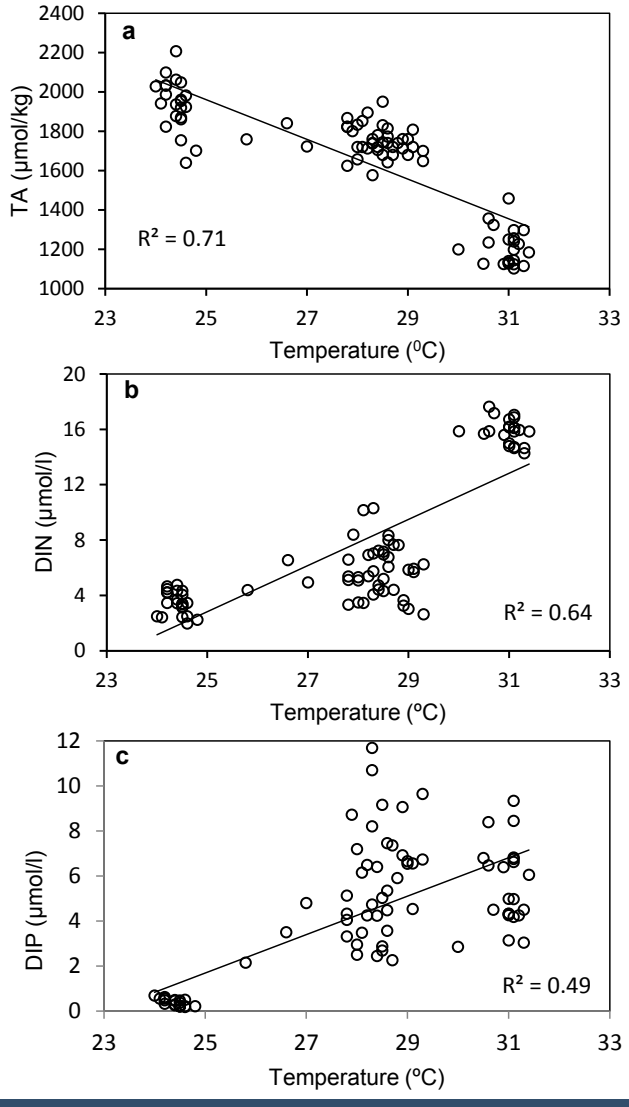

Figure 3: Relationship of temperature (°C) with a)TA (µmolkg-1), b) DIN (µmol L-1) and DIP (µmol L-1) in Mahanadi estuary during 2014.

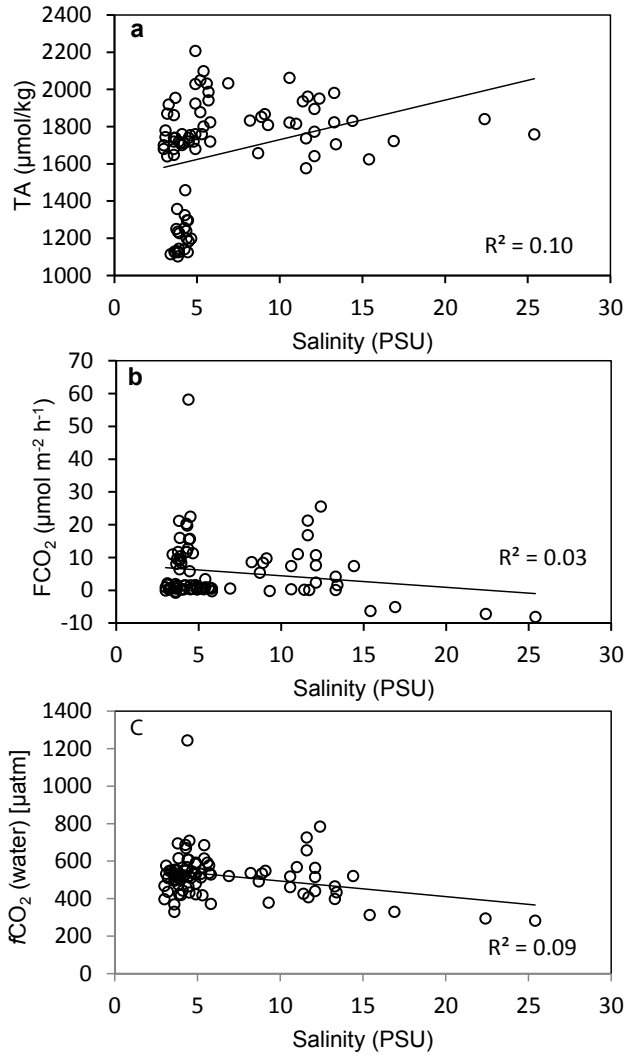

Figure 4: Relationship of salinity (PSU) with a) TA (µmol kg-1), b) FCO2 (µmol m-2 h-1) and c)fCO2 (water) [µatm] in Mahanadi estuary during 2014.

a source of CO_2. However, the majority of positive flux value suggests that the estuary acts as a strong source during pre-monsoon and monsoon while on the contrary, it acts as a weak source in winter months. This is further supported by the autotrophic nature of the Mahanadi estuary during winter months. However, Ganguly et al. [36], have shown higher efflux (611.45 m^{-2} day^{-1} during pre-monsoon in Mahanadi estuary. Other east coast estuaries namely Hooghly estuary displayed ~25.23 µmol m^{-2} h^{-1} during pre-monsoon and ~-9.05 µmol m^{-2} h^{-1} during winter [38,52].

TA and fCO_2 showed a significant negative correlation in the estuary during the observation period (Figure 5a). On the other hand, CO_2 flux density was positively correlated with fCO_2 (water) (Figure 5b). This is an indication of the fact that reduced alkalinity at higher fCO_2 is the result of the carbonic acid formation. Significant station wise variation in pH and fCO_2 was observed during the observation period in the estuary (Figure 6). The variation was more pronounced in some stations whereas less pronounced in other stations irrespective of the seasons. Minimum fluctuations of these

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parameters were observed in monsoon and post-monsoon and comparatively more fluctuations were observed in winter and summer months. Among various stations, fluctuation of a higher magnitude was observed in stations 1-3 and 10 and 11, whereas near consistency was observed among other stations. There was a significant negative relationship between fCO_2 and pH in almost all stations and consistent throughout the observation period. Minimum fluctuation of fCO_2 was observed during winter whereas maximum fluctuations were reported in the monsoon months. pH, however, had lower fluctuations among the stations and among the seasons.

Net ecosystem metabolism

The GPP of the estuary ranged between 0.05 to 1.50 mgC L^{-1} day^{-1} during the study period. As expected, GPP was high in pre-monsoon months and low in post-monsoon months. There was no significant variation in the rate of net production between post-monsoon and winter months but the amount of TOC in post-monsoon months was significantly higher (7.29 ±1.13 mg L^{-1}) than the other seasons of the year (3.20 ±0.72 mg L^{-1}). This high TOC load may be attributed to the allochathonous carbon input from surrounding terrestrial ecosystem [53,54]. The CR varied linearly with the GPP indicating high gross production in the pre-monsoon months (Figure 7). From the results, it may be inferred that the increased temperature coupled with high bacterial activity caused the sufficient release of nutrients supporting higher primary production. The assumption is supported by a high CR in the pre-monsoon months [55,20].

Conclusion

The results of the present investigation revealed that the monsoonal discharge has decisive control over the inorganic carbon components in the surface water of the Mahanadi

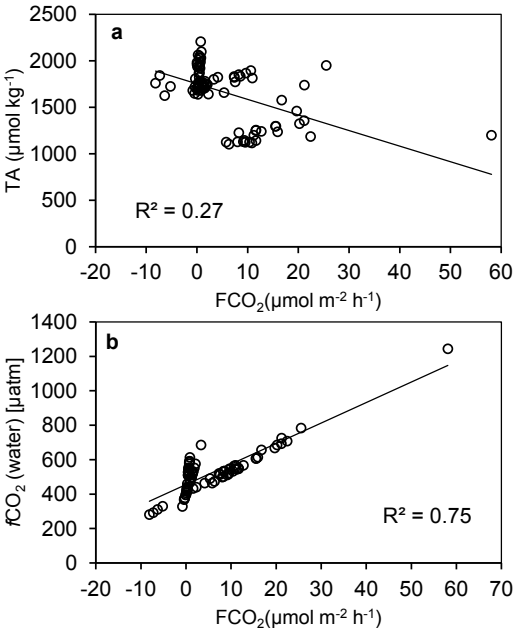

Figure 5: Relationship of a)TA (µmol kg-1) and b)fCO2 (water) [µatm] with FCO2 (µmol m-2 h-1) in Mahanadi estuary during 2014.

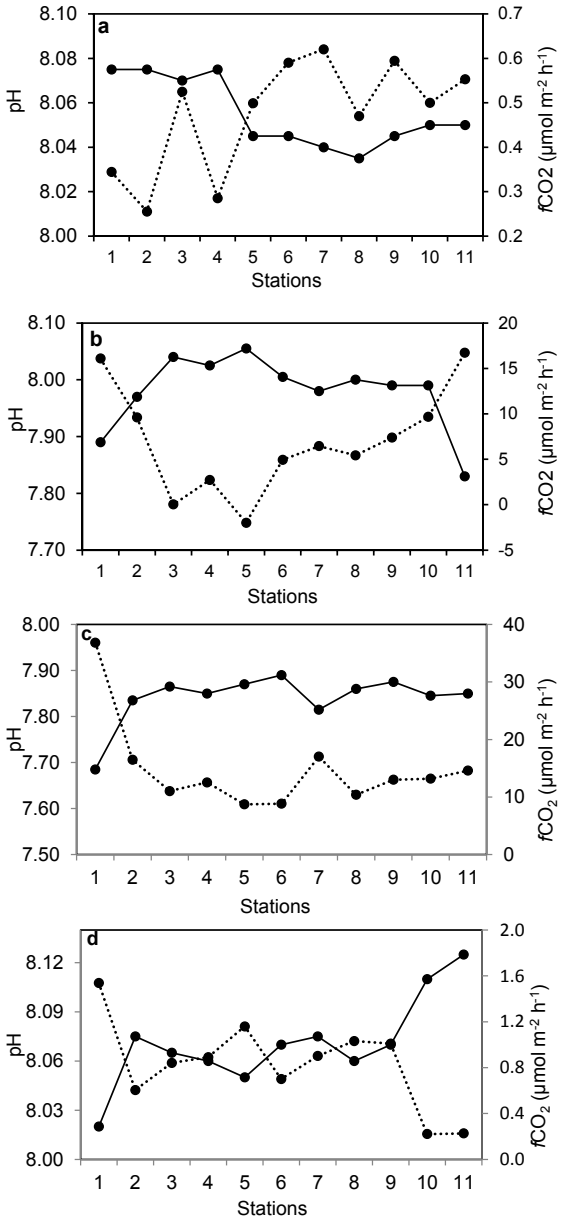

Figure 6: Variation of pH (solid line) and FCO2 (µmolm-1h-1) (dashed line) along 11 stations of Mahanadi estuary in a)Winter b)Pre-monsoon c)Monsoon d)Post-monsoon during 2014.

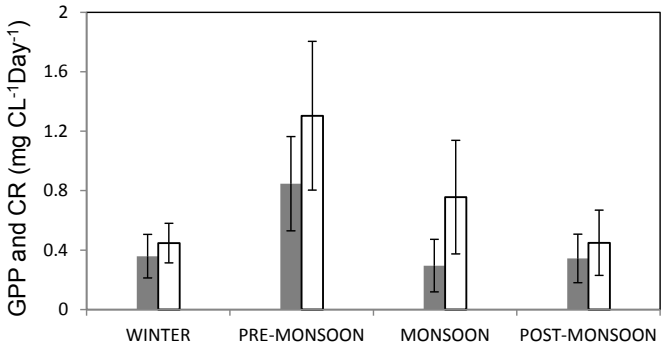

Figure 7: Seasonal variation of GPP (mgC L-1 day-1; solid) and CR (mgC L-1 day-1; empty) in Mahanadi estuary during 2014.

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estuary. The pre-monsoon period was significantly different from other seasons in terms of net ecosystem metabolism attaining higher values of GPP and CR but such gross production was not enough to maintain autotrophy. The estuary as a whole acted as a net source of CO_2 on a seasonal basis, primarily contributed by the organic carbon influx from the associated land habitats. DIC of the estuarine water depends upon the pH which is mainly regulated by evasion of CO_2, the concentration alkalinity and carbonate precipitation and dissolution. The concentrations of CO_2 and fluxes from the study sites are comparable to those estimated from the previous literature data in coastal oceans. The intra-annual variability of fCO_2 (water) has the important role in controlling the air-water CO_2 flux. It can be concluded that the source potential of the Mahanadi estuary was found to be weak in comparison with other recent studies. Temperature and salinity were the controlling factors in the biogeochemistry of carbon. The phytoplankton biomass in terms of chl *a* was found to be less in comparison to other tropical estuarine systems throughout the study period further strengthening the allochathonous organic carbon input into the estuary.

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