Variation in Carbonate System and Air-Water CO_2 Flux during Summer in the Mahanadi Estuary, India

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***Abstract*—**The carbonate system of water of the inner estuary and near shore in the Mahanadi estuary, Bay of Bengal, India was studied in summer season of 2014. Physicochemical parameters like temperature, pH, salinity, total alkalinity (TA), dissolved inorganic carbon (DIC), total organic carbon (TOC) and chlorophyll *a* (chl *a*) were measured in order to study their role in controlling the CO_2 flux. The estuary acted as a sink for atmospheric CO_2 triggered by the allochthonous organic carbon input. The average CO_2 flux was recorded as -0.36±13.29 µmol/m^2h in inner estuary and -10.36±2.00 µmol/m^2h in near shore region. The temperature and salinity were found to be significantly and positively correlated with fCO_2 (water) indicating their deterministic role in influencing air-water CO_2 flux.

***Keywords*-**Temperature, salinity, total alkalinity, air-water CO_2 flux

I. Introduction

Oceans absorb about one fourth of the anthropogenic CO_2 released to the atmosphere and acts as a CO_2 sink through biological and chemical fixation. Though open Ocean helps to mitigate the climate change by absorbing a significant portion of human driven CO_2, subsequent processes also lead to the acidification of ocean water, which has a deteriorating effect on oceanic ecosystem [1], [2]. There is a large temporal and spatial variability in CO_2 fluxes across the coastal ocean, continental shelves and open Ocean[3], [4]. The controlling factors of CO_2 fluxes vary at seasonal time scale and increase uncertainty in measurement of CO_2 fluxes. Coastal Ocean, despite being only 7% of total oceanic surface, plays an important role in global carbon cycle [5]. Bay of Bengal is a unique tropical marine system, which is more prone to pollutants as compared to the other neighbouring oceanic systems [6].The rate of decrease in pH, in temporal basis, increase the dissolved inorganic carbon, which supports the transformation of partial pressure of CO_2 in water (at low pH) thereby causing CO_2 outgassing [7]. Previous reports suggest that the coastal Bay of Bengal acts as a source for atmospheric CO_2 throughout the year except for some monsoon months [8], [9]. However, the source/sink nature and its magnitude is mainly regulated by the riverine influx and east Indian coastal current [10]. The work reported here was aimed to quantify the summer CO_2 flux in the riverine and near shore waters of Mahandi estuary and to evaluate the environmental control on CO_2 flux.

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II. Sampling And Measurements

The water sampling was carried out at 21 different stations in the Mahanadi Estuary (Figure 1), situated in the east coast of the state of Odisha (India). The inner estuary stations (station 1-12) and the near shore stations (station 13-21) are 500m and 1km distance from each other respectively. Salinity, pH and temperature were measured on site by using WTW kit (WTW model multi 340). The dissolved oxygen (DO) content of samples were immediately fixed and then determined by Winkler's method modified by Grasshoff, (1983) [11].Gross primary productivity (GPP) was measured using light and dark bottle method of Strickland & Parsons,(1972) [12].The atmospheric CO_2 was measured using Li-COR 840A. Water samples were collected using 10 L Niskin bottles at standard depth of 100cm below surface. Nutrients [dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP)] were analyzed following the standard spectrophotometric methods [11]. The pH and TA were measured in the laboratory by potentiometer (Metrohm, Switzerland)using Gran titration method following Standard Operating Procedures (SOP) suggested by DOE (1998). Total Organic Carbon (TOC) was estimated during Elementar-Vario-TOC analyzer. The water column fCO_2 and dissolved inorganic carbon (DIC) were computed using measured salinity, temperature, pH, nutrients (phosphate and silicate) CO_2 sys program [13].The wind speed data were obtained from the Indian Meteorological Department. The suspended particulate matter was measured by filtration methods implementing the gravimetric technique. Chl *a* contents of water samples were measured following the protocols of Jeffrey &Humphrey, (1975) [14]. Statistical analysis was performed using XLSTAT software.

The air-sea flux of CO_2 for the study region was calculated according to the expression

$$FCO_2 = k.\beta.\Delta fCO_2 \quad (1)$$

where 'k' is the Gas Transfer Velocity (cm/h), 'β' is the Ostwald dilution Coefficient (mol/m^3atm) and ΔfCO_2 is the differential fugacity of CO_2 between water and air, [fCO_2 (water) - fCO_2 (air)]. The gas transfer velocity was calculated using the following relation [15]

$$k = 0.17\,u_{10}\left(\frac{660}{\mathrm{Sc}}\right)^{2/3} \quad for\ u_{10} \le 3.6\,m/s \quad (2)$$

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

where u_{10} is the wind speed (m/s); Schmidt number (Sc) for CO_2 was evaluated as

The CO_2 flux in the inner estuarine system was -0.36±13.29 µmol/m^2h and in the inner shore region was -10.38±2.00 µmol/m^2h in the summer of 2014 (Table I). TA was found to be 1673±188 µmol/kg at inner estuary stations and the near shore was recorded with 1916±59.44 µmol/kg.

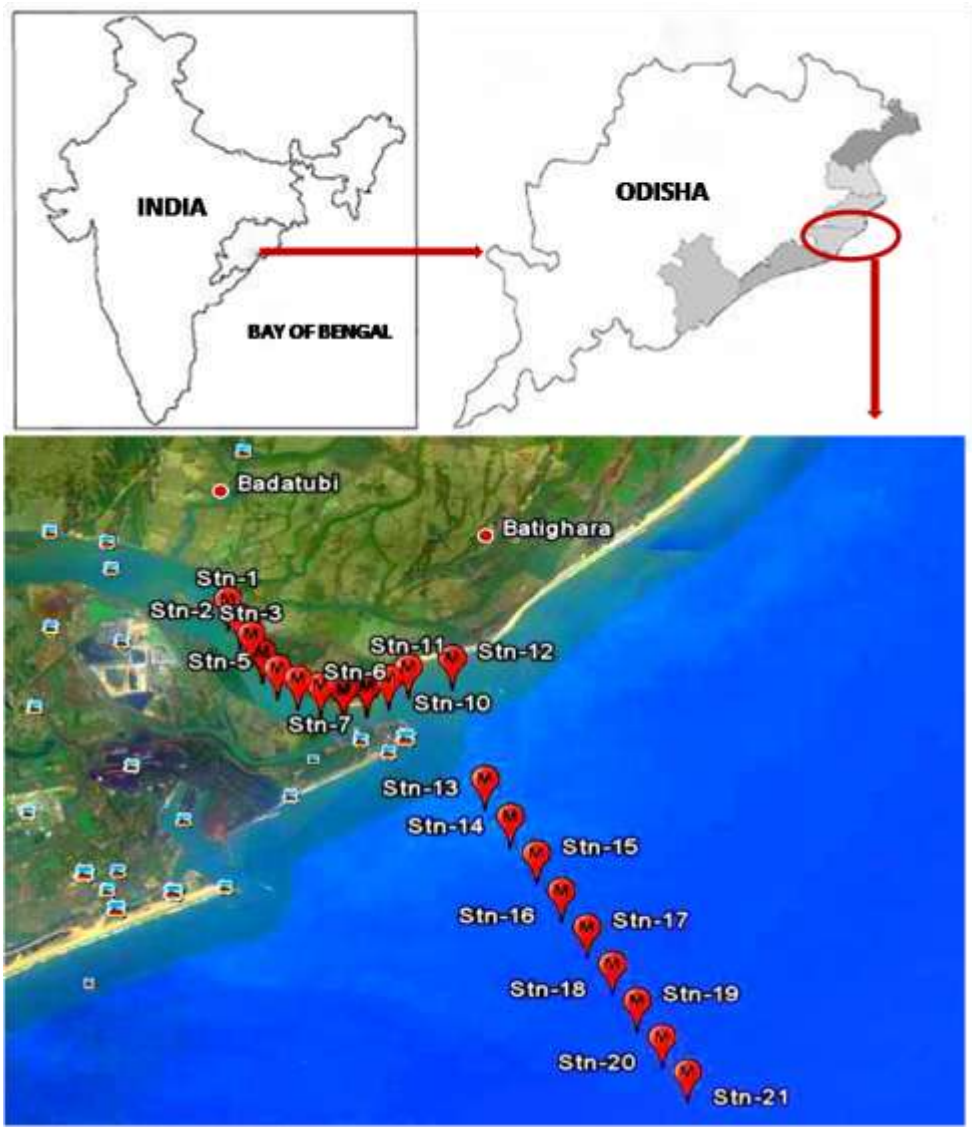

Fig. 1 Location map of the study site showing the sampling stations

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

where A = 1992.1, B = 121.86, C = 3.54, D = 0.04227 and t = Temperature (°C) of water [16].The positive magnitude of FCO_2 interprets flux from water to air and vice versa.

III. Results And Discussion

The CO_2 flux estimates from this study area falls in a range when compared to the nearby estuaries and coastal systems [17].

The fCO_2 (air) was found in a narrow range (383-396 µatm) showing minimum spatial and temporal variation. The CO_2 concentration in water was under-saturated during the study period. The fCO_2 (water) value was recorded as 390±193 µatm in the inner estuary and 233±28.90 µatm in the near shore region.

The fCO_2 (water) was found to be strongly and positively correlated (Figure 2) with temperature (r^2=0.751, n-59) and negatively correlated with salinity (r^2=0.681). The temperature and salinity have significant regulating role on carbon dynamics [18]. TOC was found higher in inner estuary (3.11±1.47 mg/l) due to the input of allochthonous organic matter. However, at near shore significantly low (2.39±0.84 mg/l) SPM followed the regular pattern of variation showing higher values in inner estuary (4231±6116 mg/l) and lower in near shore (13.85±5.55 mg/l). The variation of DO was found

to be insignificant indicating adequate mixing regime. The nitrogen and phosphorus load were found to be high in the inner estuary (5.79±1.88 µmol/land 3.90±3.00 µmol/l, respectively) whereas the near shore region was found to be nutrient poor (DIN=2.07±1.04 and DIP=0.72±0.61 µmol/l). Chl *a* was found to be significantly and positively correlated with fCO_2 (water) whereas TA showed insignificant but positive correlation with fCO_2 (water).

TABLE I
THE PHYSIOCHEMISTRY OF THE WATER SAMPLES OF MAHANADI ESTUARY (MEAN ± SD)

Parameters	Inner estuary	Near shore
Temperature (°C)	26.96±1.67	24.86±0.42
pH	8.07±0.13	8.18±0.04
Salinity (psu)	16.78±7.15	29.11±1.14
SPM (mg/l)	4231±6116	13.85±5.55
DO (mg/l)	6.94±1.31	6.95±0.48
DIN (µmol/l)	5.79±1.88	2.07±1.04
DIP (µmol/l)	3.90±3.00	0.72±0.61
Chl *a* (mg/m^3)	2.47±0.77	1.06±0.93
TA (µmol/kg)	1673±188	1916±59.44
TOC (mg/l)	3.11±1.47	2.39±0.84
DIC (µmol/kg)	1520±238	1620±61.92
fCO_2 (water) (µatm)	390±193	233±28.90
fCO_2 (air) (µatm)	391±2.23	388±3.56
FCO_2 (µmol/m^2 h)	-0.36±13.29	-10.36±2.00

A dendrogram constituting 11 measured variables related to CO_2 flux was synthesized (Figure 3) applying agglomerative hierarchical clustering (AHC). The dendrogram represents three clusters and the 2nd cluster is the most important cluster comprising 5 groups.

The appearance of fCO_2 (water) and air-water CO_2 flux in one group having the least Euclidian distance denoted that the flux density was mainly regulated by fCO_2 (water). The DIC and TA were found to be conserved in nature. The GPP was more or less influenced by temperature in tropical bodies though the relationship was not as strong as that of subtropical and temperate oceans. Nevertheless primary production was encouraged by increase in temperature due to a better availability of nutrients generated by the augmented bacterial activity. Thus increase in temperature to some extent influenced the CO_2 regime of surface water and made it a sink by enhanced primary production [19].

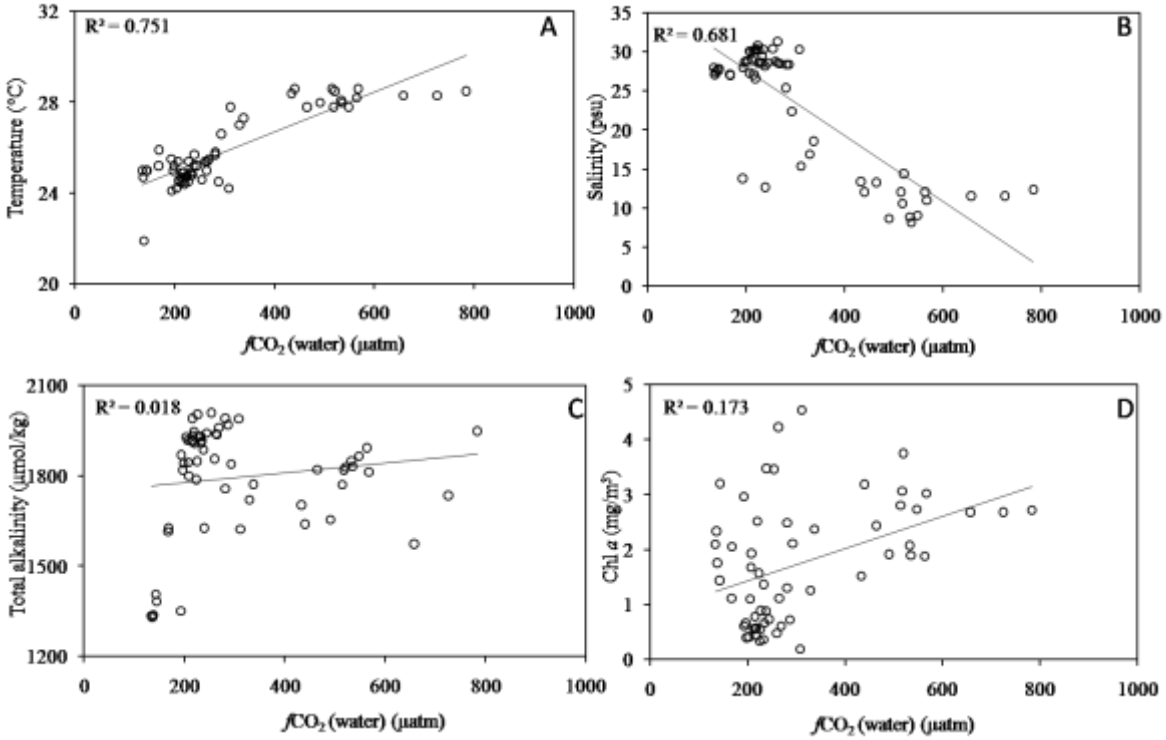

Fig. 2 Relationship of A- SST (°C), B- Salinity (psu), C- TA (µmol/kg) and D- Chl *a* with fCO_2 (water) (µatm)

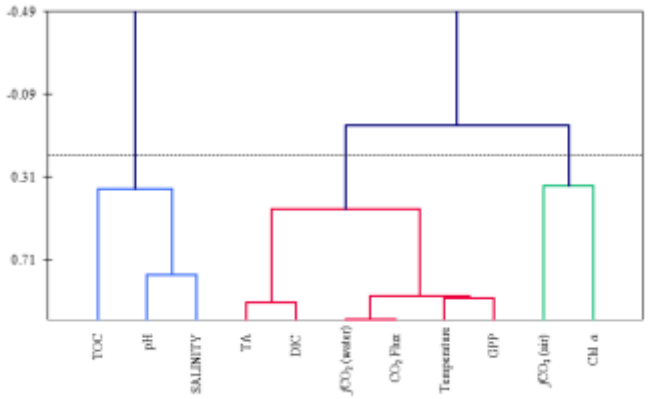

Fig. 3 Dendrogram showing the contribution of the measured parameters to CO_2 flux in the Mahanadi estuary

IV. Conclusion

The study established that the Mahanadi Estuary was a sink of CO_2 in summer, 2014 as during summer, primary production in the surface ocean promoted atmospheric CO_2 uptake. The inner estuarine zone was found to be a lesser sink as compared to the near shore region. The flux density was mainly regulated by the ΔfCO_2 rather than gas transfer velocity.

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