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SEASONAL VARIABILITY OF ACIDIFICATION IN MAJOR ESTUARIES OF INDIAN SUNDARBANS

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ABSTRACT
We analysed the Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA) and pH of the aquatic phase of the Hooghly and the Matla estuaries during 1984 to 2018 through seasons. A unique seasonal trend is observed for all these variables with maximum during premonsoon, followed by postmonsoon and monsoon. The relatively higher values of DIC, TA and pH in the Canning Station along the Matla estuary may be attributed to minimum head on discharge in this tide fed river. The lowering of pH in both the estuaries may however, pose an adverse impact on the biotic community especially with calcareous shell. This might create an ecological imbalance in the food webs of this mangrove dominated World Heritage Site.

***Keywords**: Dissolved Inorganic Carbon, Total Alkalinity, pH, Sagar South, Canning, Indian Sundarbans.*

I. INTRODUCTION

The rapid pace of industrialization and urbanization has significantly altered the level of CO_2 in the atmosphere. The present CO_2 level in the atmosphere is 413.09 ppm which is about 68.85 ppm more than the level in 1984[1]. Indian Sundarbans at the apex of Bay of Bengal is no exception to this rule [2]. The study reported that atmospheric CO_2 exhibited the lowest value of 384.98 ppm (during premonsoon 1984) to 405.09 ppm (during post monsoon 2016), which is an increase of 5.22% over a period of more than three decades. Alteration in the level of atmospheric CO_2 changes the constituents of marine and estuarine water in terms of Total Alkalinity (TA), Dissolved Inorganic Carbon (DIC) and pH. To investigate the seasonal variation of inorganic carbon system in the Hooghly and the Matla estuaries of Indian Sundarbans DIC, TA and pH were measured along the two estuaries from 1984 to 2018 through seasons.

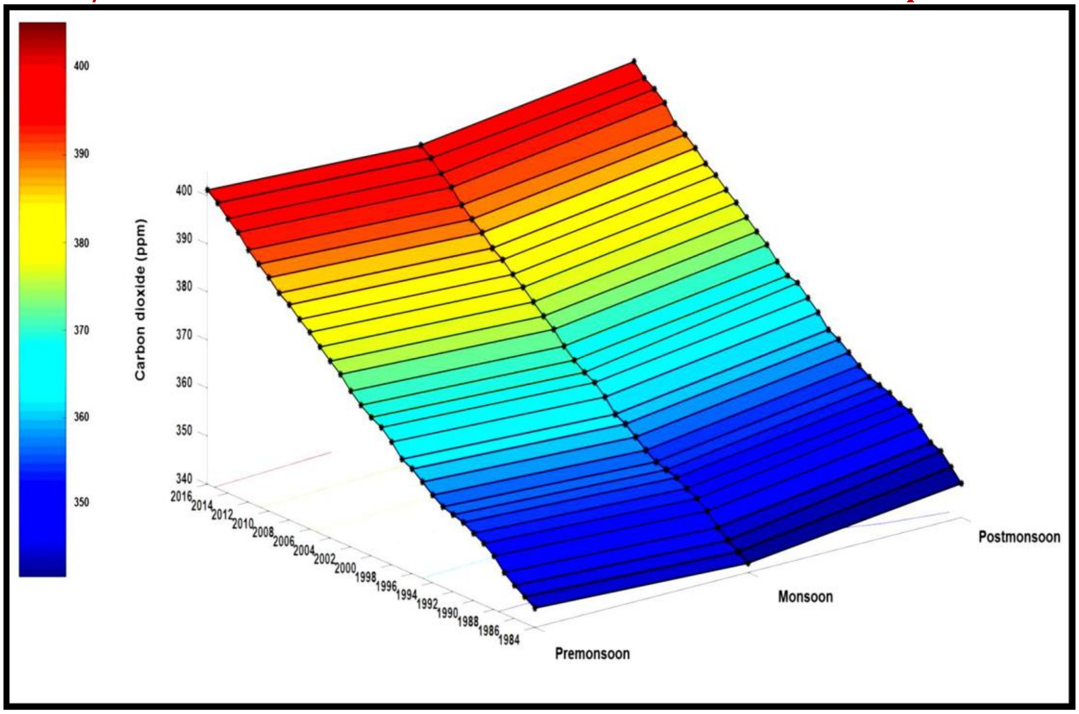

Figure 1: Spatio-temporal variation of carbon dioxide

II. MATERIALS & METHOD

Study Area

The present study was carried out at two major estuaries of Indian Sundarbans namely Hooghly in the western most part of Indian Sundarbans and the Matla estuary in the central sector of Indian Sundarbans. Two stations Sagar South (88°04' 0.51" E 21° 37' 49.90"N) and Canning (88°41' 04.43" E 22° 19' 03.20"N) were selected along the Hooghly and Matla estuaries respectively.

Sagar South is situated on the south western part of the Sagar Island at the confluence of the River Hooghly and the Bay of Bengal. It is an anthropogenically stressed zone due to the presence of passenger jetties, fishing activities and pilgrimage. Canning is situated in the central part of Indian Sundarbans and faces the River Matla, a tide fed river. Due to presence of fish landing station, passenger jetties and busy market in the area it is also a stressed zone. The present work of estimating DIC, TA and pH were carried out during 1984 to 2018 in the months of April (premonsoon), August (monsoon) and December (postmonsoon) during the entire tenure of the work.

Analytical Methods

DIC and TA samples were filtered through a cellulose acetate filter (0.45 µm) into 250 mL borosilicate bottles, fixed with100µL of saturated mercury bichloride solution, preserved at 4 °C, and analyzed within 96 hrs of sample collection[3,4]. DIC was determined *via* acid extraction by quantifying the released CO_2 using an infrared gas analyzer (AS-C3, Apollo SciTech). TA was measured by Gran titration [5] using an open-cell semiautomatic titration system (AS-ALK2, Apollo SciTech) [6, 7].

In situ analysis of surface water pH was carried out using a portable pH meter (sensitivity= ±0.02) after standardizing the same with pH buffer of 4.00 and 7.00.

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III. RESULTS

Spatio-temporal variations of DIC, TA and pH

In both the estuaries, DIC exhibited significant variations between years and seasons (Tables 1 & 2).The trend is similar for Total Alkalinity (Tables 3 &4) and pH (Tables 5 & 6).

It is interesting to note that DIC follows a unique seasonal trend in both the stations and the order is premonsoon (mean value: 1418 $\mu molkg^{-1}$) > postmonsoon (mean value: 1382 $\mu molkg^{-1}$) > monsoon (mean value: 1336 $\mu molkg^{-1}$) at Sagar South. For Canning, the sequence is premonsoon (mean value: 1936 $\mu molkg^{-1}$) > postmonsoon (mean value: $\mu molkg^{-1}$) > monsoon (mean value: $\mu molkg^{-1}$).

Table 1 ANOVA of DIC at Sagar South

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Years	7471364	34	219746	73.05376	9.6E-42	1.601159
Between Seasons	117710.4	2	58855.21	19.5662	1.94E-07	3.131672
Error	204544.2	68	3008.004			
Total	7793618	104				

Table 2 ANOVA of DIC at Canning

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Years	1887777	34	55522.85	70.89833	2.55E-41	1.601159
Between Seasons	80377.6	2	40188.8	51.31795	2.6E-14	3.131672
Error	53253.07	68	783.1333			
Total	2021407	104				

Table 3 ANOVA of TA at Sagar South

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Years	20945.26	34	616.037	16.7226	8.06E-22	1.601159
Between Seasons	87957.51	2	43978.75	1193.823	1.1E-53	3.131672
Error	2505.024	68	36.83859			
Total	111407.8	104				

Table 4 ANOVA of TA at Canning

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Years	36356.75	34	1069.316	58.21776	1.54E-38	1.601159
Between Seasons	58297.87	2	29148.94	1586.982	8.67E-58	3.131672
Error	1248.992	68	18.36752			
Total	95903.61	104				

Table 5 ANOVA OF pH at Sagar South

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Years	0.564063	34	0.01659	85.42709	5.69E-44	1.601159
Between Seasons	0.018194	2	0.009097	46.84379	1.62E-13	3.131672
Error	0.013206	68	0.000194			
Total	0.595463	104				

Table 6 ANOVA OF pH at Canning

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Years	0.06933	34	0.002039	22.84154	8.43E-26	1.601159
Between Seasons	0.004396	2	0.002198	24.62253	9.04E-09	3.131672
Error	0.00607	68	8.93E-05			
Total	0.079796	104				

In case of total alkalinity the seasonal trend is similar with highest value during premonsoon at Sagar South (mean value: 162.74mg/L) and at Canning (mean value: 170.06mg/L) followed by postmonsoon at Sagar South (mean value: 127.87mg/L) and at Canning (mean value: 149.75mg/L) followed by monsoon at Sagar South (mean value: 93.86mg/L) and at Canning (mean value: 113.12mg/L).

In case of pH the seasonal trend is similar to that of DIC content and TA. For Sagar South the mean value of pH was 8.25 during premonsoon, 8.23 during postmonsoon and 8.21 during monsoon season. For Canning the mean values were found be 8.31, 8.30 and 8.29 during premonsoon, postmonsoon and monsoon seasons respectively.

IV. DISCUSSION

Total alkalinity (TA) is defined as TA = $[HCO_3^-] + 2[CO_3^{2-}]$ plus all other weak bases that can accept H^+ when titrated to the carbonic acid endpoint. Comparably, dissolved inorganic carbon (DIC) is expressed as the sum of all inorganic carbon species ($[CO_2]$, $[HCO_3^-]$,$[CO_3^{2-}]$). In terrestrial aquatic systems, there are three sources of dissolved inorganic carbon. The most important sources are from the carbonate and silicate weathering processes as described below:

$$CaCO_3 + CO_2 \rightarrow 2\ HCO_3^- + Ca^{2+} \quad (1)$$

$$CaSiO_3 + 2CO_2 + 3H_2O \rightarrow 2\ HCO_3^- + Ca^{2+} + H_4SiO_4 \quad (2)$$

In both cases, the amounts of DIC and TA production are equal. Here, CO_2 may come from soil organic matter respiration but ultimately it is linked to the atmospheric CO_2.

Typically, the supply of inorganic carbon by rivers to the coastal ocean is governed by river discharge, weathering intensity, and the geology of the drainage basin [8-10]. The weathering of carbonate and silicate minerals consumes atmospheric CO_2 and transports HCO_3^- ions and subsequent cation and anion products into oceanic systems. Eventually, CO_2 is released back into the atmosphere *via* oceanic carbonate sedimentation and volcanic activity [11, 12]. Guo et al. [10] found that, in the Pearl River estuary, DIC and TA values were substantially lower during the wet season (~1000 and 700 $\mu molkg^{-1}$, respectively) than during the dry season (> 2700 and > 2400 $\mu molkg^{-1}$,respectively). They suggested that the much lower DIC and TA values in the wet season were a result of increased river discharge diluting overall production of DIC and TA by weathering and decomposition. Similar results were found in the Mississippi and Changjiang where river HCO_3^- concentration and discharge are negatively correlated [13, 14].

In the present study the lowest value of DIC and TA during monsoon may be attributed to discharge from the Farakka Barrage situated in the upstream region of Ganga-Bhagirathi-Hooghly river system. Ten year survey (1999-2008) on water discharge from Farakka dam revealed on average discharge of (3.7 ± 1.15) $X10^3\ m^3s^{-1}$. Higher discharge values were observed during the monsoon with an average of (3.81 ± 1.23) × $10^3\ m^3s^{-1}$and the maximum of the order 4524 m^3s^{-1}during freshet (September). Considerably lower discharge values were recorded during premonsoon with an average of (1.18 ± 0.08) × $10^3\ m^3s^{-1}$and the minimum of the order 846 m^3s^{-1} during May. During postmonsoon discharge, values were moderate with an average of (1.98 ± 0.97) × $10^3\ m^3s^{-1}$ [15].

The values of DIC, TA and pH are relatively higher in the water around the Canning station mainly because of the location of the station along the Matla estuary. The estuary is hyper saline in nature compared to Hooghly estuary mainly because of the blockage of the fresh water from the upstream region due to siltation. [16-21] The Matla estuary in an ideal sense cannot be considered as estuary as there is no mixing of fresh water due to blockage caused by siltation. It is basically a tide fed river whose survival is a function of tides form the Bay of Bengal and hence in the absence of dilution with fresh water the values of DIC, TA and pH are relatively higher.

Negative correlation between TA and river discharge has been observed for other river systems such as the Mississippi, Changjiang, Pearl, Huanghe, Congo, and Indus [22-27, 10]. The increasing trend of DIC, TA and pH in the Matla estuary may be the impact of almost zero riverine discharge from the upstream region unlike the Hooghly estuary where the lowering of pH is more pronounced.

To summarize it can be stated that the lowering of pH in the Hooghly estuary has been calculated to be 0.0076/year during premonsoon, 0.0091/year during monsoon and 0.0079/year during postmonsoon and that in the Matla estuary the values were found to be 0.0029/year 0.0038/year and 0.0032/year for premonsoon, monsoon and postmonsoon respectively. This is an indication of acidification which has serious implication on the biotic community especially the molluscan community which is abundant in the present geographical locale. The gradual extinction or disturbance on the molluscan community may disrupt the food chain/webs spun in this mangrove ecosystem since long evolutionary period of time as these are filter feeders and regulate the plankton biomass at the base of the food chain/web.

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