

COMPARATIVE STUDY OF CARBON DIOXIDE SYSTEM IN VIRGIN AND RECLAIMED MANGROVE WATERS OF SUNDARBANS DURING FRESHET

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ABSTRACT

Diurnal changes in temperature, salinity, dissolved oxygen, $p\text{CO}_2$, (HCO_3^-) (CO_3^{2-}) and ionic product of calcium carbonate were studied in virgin and reclaimed mangrove waters of Sundarbans during monsoonal run off. Surface water of both the places was undersaturated with respect to oxygen and partial pressure of carbon dioxide remained high. Lower calcium/chlorinity values than those in the open ocean were obtained. Considering high $p\text{CO}_2$ & changes in calcium/chlorinity ratio between day and night, possibilities of precipitation or dissolution of calcium carbonate were examined.

Key-words: Sundarbans, carbon dioxide system.

INTRODUCTION

Study of carbon dioxide system is especially interesting in view of the controversies in water pollution studies, as to whether carbon dioxide or phosphorous is the major limiting factor in fresh water and therefore, the key constituent in the process of cultural eutrophication (Kuentzel, 1969; Lange, 1967). Carbon dioxide, like oxygen may be present in water in highly variable amounts but its behaviour in water is rather different and its impact on ecosystem has not been adequately conceived. It is, therefore, difficult to make general statement on its role as a limiting factor (Odum, 1971).

The ecology of the Hooghly estuary has been subjected to major change after the commissioning of the Farakka Barrage on the Ganga on 21st April, 1975. Observations on the ecological changes in Hooghly estuary were made by Nandi, Bagchi and Majumder (1983) to estimate the effect of fresh water release. During freshet, when the fresh water outflow is at its maximum, the decomposed organic matter carried by flood waters into the riverine system reaches a high level which is supposed to gear up the carbon dioxide system substantially. A summary of the large-scale variations in partial pressure of CO_2 in surface oceanic waters and their relationship to patterns of oxidation is given by Skirrow (1975). Adequate attentions were not paid to this effect by the previous workers

(Bhunia and Choudhury, 1982; Nandi, Bagchi and Majumder, 1983). Seldom any observation has been made on variations in partial pressure of CO_2 in mangrove waters which is of importance in the ecology of deltaic Sundarbans. This prompted to study and to compare the carbon dioxide system at two stations — one in a reclaimed area, River Mooriganga ($21^\circ 52'N$ and $88^\circ 16'E$) where the fresh water flows in larger proportion and another in a virgin area, River Saptamukhi ($21^\circ 43'N$ and $88^\circ 18'E$) where fresh water discharge is less, during 9-12 August, 1986. The station positions are shown in Fig. 1.

MATERIALS AND METHODS

Water samples were collected from one meter depth using Nansen bottle every three hours over a 24 hr. period during 9-10 August, 1986 at Saptamukhi (8m depth) & 11-12th August, 1986 at Mooriganga (10m depth). The parameters measured were temperature, salinity dissolved oxygen, pH, alkalinity, calcium-magnesium and primary productivity. Two sets of samples were stored in well sealed plastic bottles and brought to the shore laboratory where calcium and magnesium were determined by the method of Culkun and Cox (1986). The precision of this method has been found to be $\pm 0.38\%$ (Sen Gupta, Naik and Singbal, 1978). Salinity and dissolved oxygen were measured by standard analytical methods (Grasshoff, Ehrhardt and Kremling, 1983). pH was measured with a portable battery operated pH meter (Sensitivity ± 0.02 pH Unit). Alkalinity

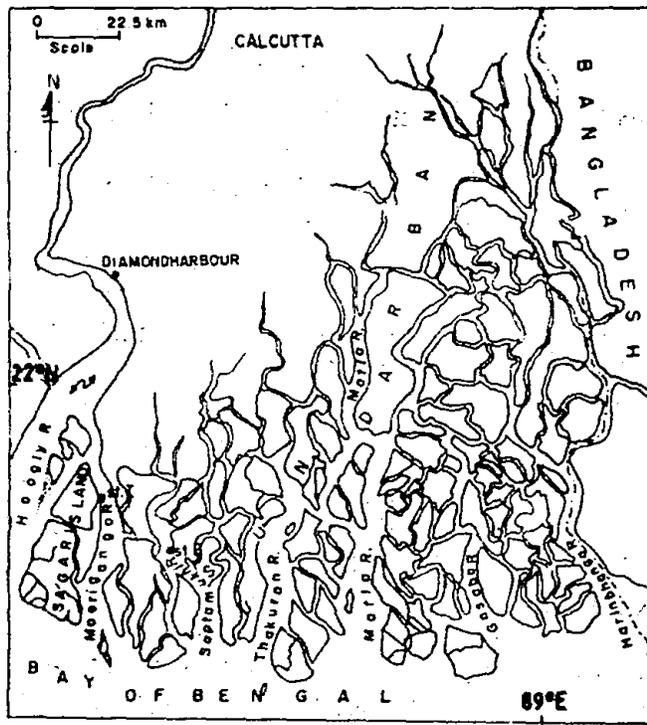


Fig. 1. Map showing station locations.

was determined by the pH method of Anderson and Robinson as modified by Culberson, Pytkowicz and Howley (1970). Values of pk'_1 & pk'_2 of carbonic acid given by Plath, Johnson and Pytkowicz (1980) were used for the calculation of carbonate and bicarbonate concentrations. For solubility coefficient of carbon dioxide the formula provided by Weiss (1974) was used to calculate pCO_2 . A plot of $\Delta pH/\Delta v$ versus v was used to evaluate the completion of titration. Since most pH values lie in between 7.35 and 7.95 and contribution of the borate ion to total alkalinity is significant at pH value above 8, it is therefore, ignored here (Riley and Chester, 1971). Primary productivity was determined by the oxygen bottle method (Strickland and Parsons, 1968).

RESULTS AND DISCUSSION

One set of observations of the time-variable chemical parameters during 9-12 August, 1986, at Saptamukhi and Mooriganga over 24 hours at each station is presented in Figs. 2 & 3. It was found that salinity at Mooriganga varied between 2.48×10^{-3} and 9.89×10^{-3} whereas at Saptamukhi it was between

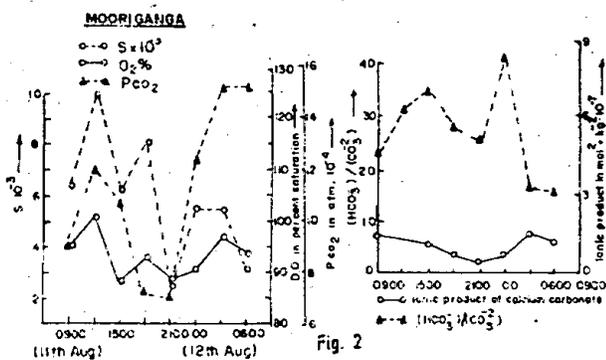


Fig. 2

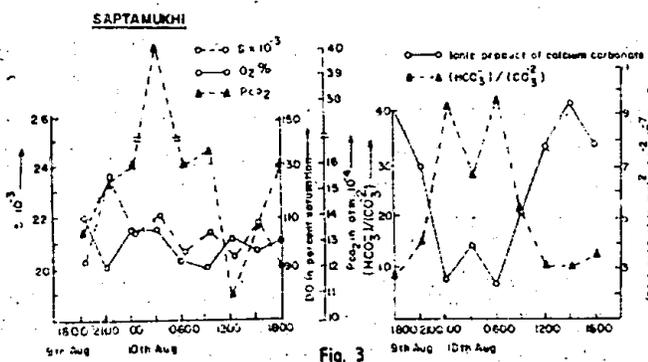


Fig. 3

Figs. 2 & 3. Diurnal variation of pCO_2 , ionic product of calcium carbonate and bicarbonate-carbonate ratio in River Mooriganga & Saptamukhi resply.

19.98×10^{-3} and 23.55×10^{-3} indicating less dilution in this region during the fresher time compared to Mooriganga area. Dissolved oxygen calculated in terms of percentage saturation showed inverse correlation with salinity at the Saptamukhi Station (Fig. 3). Percentage saturation of oxygen increased from 90.1 to 100.6 when salinity decreased from 23.55×10^{-3} to 19.98×10^{-3} at the Saptamukhi Station. But the situation was observed to be different at Mooriganga where dissolved oxygen increased when salinity increased and decreased when salinity also decreased indicating that the incoming fresh water was less saturated with respect to oxygen (Fig. 2). Percentage saturation of oxygen decreased from 100.8 to 98.3 when salinity also decreased from 9.89×10^{-3} to 2.48×10^{-3} . The depletion of oxygen can be expected to occur in the upper reaches of the Hooghly river as a result of sewage discharge, virtually without any treatment (De, 1986). Partial pressure of carbon dioxide was observed to be very high, specially at Saptamukhi where dilution was less. It showed a maximum value of 39.99×10^{-4} atm. 0300 hrs. and a minimum value of 10.822×10^{-4} atm. at 1200 hrs when oxygen also showed a increasing trend. This could be due to biodegradation of organic matter in the water column. The total difference between night and day time was 29.17×10^{-4} atm.

Although temperature is one of the factors which influences the variation of $p\text{CO}_2$ (Takahashi, 1961), yet the variation of the average surface temperature during the tidal cycle between day and night time at both the stations was only less than 1°C . At Mooriganga $p\text{CO}_2$ also showed a high value of 15.26×10^{-4} atm. at 0300 hrs. The average value of the $p\text{CO}_2$ was 17.19×10^{-4} atm. at 30.7°C and average value of percentage saturation of oxygen was 98.9 at Saptamukhi. At Mooriganga, average value of $p\text{CO}_2$ was 11.14×10^{-4} atm. and percentage saturation of oxygen was 93.57 at 29.9°C . At both the places surface water remained under-saturated with respect to oxygen and the partial pressure of carbon dioxide remained high. For oxygen saturation the critical value of "t" obtained from the table (2.101) at 0.05 probability level is lower than the observed value of 4.07. For $p\text{CO}_2$ the critical value of "t" (2.11) at 0.05 probability level is also lower than the observed value of 2.42. Therefore, the difference between the virgin and stressed environments are significant. The gross and net productivity at Saptamukhi were observed as $77.9 \text{ mgC m}^{-3} \text{ hr}^{-1}$ and $58.1 \text{ mgC m}^{-3} \text{ hr}^{-1}$ whereas at Mooriganga the corresponding values were $19.58 \text{ mgC m}^{-3} \text{ hr}^{-1}$ and $9.69 \text{ mgC m}^{-3} \text{ hr}^{-1}$ respectively while the climatic conditions at both the places were similar. This indicates that the low saline area becomes less productive due to high turbidity and less penetration of light.

The effect of high $p\text{CO}_2$ was observed in the calcium carbonate saturation. The calcium/chlorinity ratio for the samples from Saptamukhi and Mooriganga were found to be 0.01718 ± 0.000143 and 0.02209 ± 0.00050 respectively with an average calcium concentration of $4.992 \times 10^{-3} \text{ mol/kg}$ and $1.5554 \times 10^{-3} \text{ mol/kg}$. These values are low compared to the open sea as reported by Sen Gupta, Naik and Singhal (1978). The lowering of the levels of calcium in the Mandovi and Zuari estuary was also observed during the monsoon

months by Sen Gupta and Naik (1981). Since the calcium concentration at the source was not estimated, a definite conclusion regarding its semi-conservative nature could not be drawn here.

Dissolved oxygen varied from 112.2% at 1800 hrs to 93.8% at 0600 hrs. at Saptamukhi which indicates the effect of increase in intensity of respiratory processes during night and absence of photosynthesis. At Mooriganga this difference was not significant.

To study the effects of these processes on the dissolution and precipitation of calcium carbonate, the degree of saturation was calculated by using the equation given by Ingle (1975), for samples from Saptamukhi station where the average degree of saturation with respect to calcite decreased steadily from 12 during day time to 6 during night time. For samples from the Mooriganga station the equation was not applicable due to low salinity value. Therefore, the ionic product of CaCO₃ and (HCO₃⁻)/ (CO₃⁻²) have been compared with time and presented in Figs. 2&3. Thus it may be inferred that, inspite of high pCO₂ and (HCO₃⁻)/ (CO₃⁻²) ratio at night the water remained at least six fold supersaturated with respect to calcite. At Mooriganga Ca/Cl ratio showed higher value than Saptamukhi due to decrease in salinity and the variation in ionic product of calcium carbonate and (HCO₃⁻)/ (CO₃⁻²) ratio showed predominance of tidal influence (Fig. 2). It was observed that average maximum buffer index of bicarbonate (βHCO_3^-)_{max}, was 3.32 times greater than the maximum buffer index of carbonate, (βCO_3^{2-})_{max} at Saptamukhi whereas (βHCO_3^-)_{max} was 4.37 times greater than (βCO_3^{2-})_{max}, at Mooriganga.

Usually those organisms which use calcium carbonate are most abundant where the partial pressure of CO₂ is low. Also the successful precipitation of calcium carbonate depends upon the equilibrium, $\text{Ca}^{+2} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ and is favoured by high (Ca⁺²) and low (CO₂). In both environments (Ca⁺²) is low and pCO₂ is high indicating less possibility of precipitation. The increase of the calcium/chlorinity ratio for the samples from Mooriganga during the night time were found to be 0.26%. No significant difference in calcium/chlorinity ratio between day and night time for samples from Saptamukhi was observed. Therefore, the decrease in supersaturation was due to the increase of pCO₂ and not due to precipitation.

The spontaneous precipitation of calcium carbonate is very slow in sea water, apparently because of the presence of Mg⁺² ion which strongly impedes the growth of CaCO₃ crystals. Only 9% of CO₃⁻² in sea water occurs in the free form, 7% in combination with Ca⁺² and a very high proportion (67%) with Mg⁺² (Garrles and Thompson, 1962). The ion pair would have to be extensively broken up for calcium carbonate to form spontaneously. The magnesium/chlorinity ratios for the samples from Saptamukhi and Mooriganga were found to be

0.05671 \pm 0.002 and 0.05689 \pm 0.0241 respectively with an average magnesium concentration of 2.74×10^{-2} mol/kg and 0.67×10^{-2} mol/kg. Therefore the possibility of dissolution of calcium carbonate at Mooriganga during night time may not be completely ruled out.

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