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The postmonsoon carbon biogeochemistry of estuaries under different levels of anthropogenic impacts

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Abstract

The different aspects of carbon biogeochemistry were studied during the postmonsoon at the Hooghly-Sundarbans estuarine system, a part of the Ganga-Brahmaputra river system located in the northeastern India. The study focused on understanding the differences in carbon biogeochemistry of estuaries undergoing different levels of anthropogenic stress by investigating anthropogenically influenced Hooghly estuary and mangrove-dominated estuaries of the Sundarbans. The salinity of well oxygenated (%DO: 91 - 104%) estuaries of the Sundarbans varied over a narrow range (12.74 - 16.69) during postmonsoon relative to the Hooghly (0.04 - 10.37). Phytoplankton productivity and carbonate precipitation and/or dissolution were dominant processes controlling DIC dynamics in different parts of the Hooghly, whereas signal for mangrove derived DIC removal was observed in the Sundarbans. Influence of groundwater on estuarine DIC biogeochemistry was also observed in both the estuaries with relatively higher influence at the Hooghly than Sundarbans. In both estuarine systems, DOC behaved non-conservatively with ~ 40% higher DOC level in the Hooghly compared to the Sundarbans. No significant evidence of phytoplankton production on DOC level was found in these estuaries, however signal of DOC input through pore-water exchange at the Sundarbans was observed. Relatively lower $\delta^{13}C_{POC}$ at the Hooghly compared to the Sundarbans suggest relatively higher terrestrial influence at the Hooghly with a possibility of *in situ* biogeochemical modifications of POC at the Sundarbans. The freshwater run-off coupled with *in situ* aerobic OC mineralization controlled estuarine pCO_2 level at the Hooghly, whereas the same was principally exogenous for the Sundarbans. The entire Hooghly-Sundarbans system acted as source of CO_2 to the regional atmosphere with ~17 times higher emission from the Hooghly compared to Sundarbans. The present study clearly establishes the dominance of anthropogenically influenced estuary over relatively pristine mangrove dominated one in the regional greenhouse gas budget and climate change perspective.

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1 Introduction

Estuaries connecting terrestrial and marine ecosystems record biogeochemical and hydrological processes operating between these two environments. Estuaries play an important role in modulating global carbon (C) cycle and anthropogenic carbon dioxide (CO_2) budget (Bauer et al., 2013; Regnier et al., 2013; LeQuéré et al., 2016). Atmospheric CO_2 is sequestered into terrestrial systems through photosynthesis and weathering reactions and is transported to the ocean via rivers and estuaries. About $1x10^{15}$ g of C is discharged annually from the land to the ocean through rivers and estuaries (Degens et al., 1991). Around 40 % of this C is discharged as dissolved inorganic carbon (DIC) and the rest as dissolved organic carbon (DOC) and particulate organic carbon (POC) (Richey et al., 2002). Although estuaries are only ~ 4% of the continental shelf regions, CO_2 emission flux from estuarine surface waters is as high as CO_2 uptake in continental shelf regions of the world (Borges et al., 2005; Chen and Borges, 2009; Cai et al., 2006; Cai, 2011) suggesting estuaries to be not only active pathway for transport of C (Ittekkot and Laane, 1991) but also a hotspot for biogeochemical modification of organic matter (OM) (Frankignoulle et al., 1998).

Mangroves covering 137,760 km^2 along tropical and sub-tropical estuaries and coastlines (Giri et al. 2011) are among the most productive natural ecosystems in the world with net primary productivity of 218 ± 72 Tg C yr^{-1} (Bouillon et al. 2008a). The biogeochemical characteristic of a mangrove-dominated estuary is largely different from anthropogenically polluted estuary, where much of the OM is derived from domestic, agricultural and industrial wastes. In anthropogenically affected estuarine systems, heterotrophy generally dominates over autotrophy (Heip et al., 1995; Gattuso et al., 1998) and a substantial fraction of biologically reactive OM gets mineralized within the system (Servais et al., 1987; Ittekkot, 1988; Hopkinson et al., 1997; Moran et al., 1999). Our understanding about transformation of mangrove derived C and its subsequent export to the adjacent aquatic system appears to be limited, particularly when mangroves are disappearing at alarming rates worldwide (Dittmar and Lara, 2001a; 2001b). A significant fraction of mangrove sequestered C is supplied to intertidal mangrove sediment via litter fall, which undergoes biogeochemical transformations leading to emission of trace gases, like CO_2 and CH_4, from sediments. The rest is exported to adjacent coastal waters or gets buried in sediment layers as long-term sequestration (Jennerjhan and Ittekkot 2002; Barnes et al., 2006; Kristensen and Alongi, 2006; Donato et al., 2011; Linto et al., 2014). Apart from lateral transport of dissolved and particulate C, biogeochemical processes, such as primary

production, OM mineralization, $CaCO_3$ precipitation / dissolution and water-atmosphere CO_2 exchange, occurring in the estuarine water column also regulates inorganic and organic C biogeochemistry of a mangrove-dominated estuary. These processes largely depend upon pH, nutrient availability, euphotic depth variability as well as planktonic and bacterial biodiversity and community compositions. Lack of ample quantitative estimation of above-mentioned biogeochemical processes in many regions of the world restrains mangrove biogeochemists from an in depth understanding of these processes, which also leads to uncertainty in estimation of coastal C biogeochemical budget on global scale.

In India, research related to C biogeochemistry of estuarine ecosystems have been in focus since last two decades with emphasis on estuaries located in the southern India (e.g., Bouillon et al., 2003; Sarma et al., 2012; Sarma et al., 2014; Bhavya et al., 2017; Bhavya et al. 2018). During the present study, we focused on C biogeochemical differences of two adjacent estuarine systems, i.e., the estuaries of Sundarbans and Hooghly estuary, which are part of Ganga-Brahmaputra river system located in the northeastern India. Characteristically, these two estuaries are very different from each other with the estuaries of Sundarbans being mangrove-dominated and Hooghly as anthropogenically influenced. Biogeochemical studies in these estuaries are limited to rudimentary measurements with focus on trace gases (Mukhopadhyay et al., 2002; Biswas et al., 2004, 2007; Dutta et al., 2013, 2015a, 2015b, 2017; Ganguly et al., 2008, 2009), with exception of one comprehensive nutrient budget at the Hooghly estuary (Mukhopadhyay et al., 2006). One of the major drawback of these studies are limited number of sampling locations. Given the vast expanse of these estuaries, extrapolation of data from these studies for the entire ecosystem may lead to overestimation/underestimation. During the present study, we focused on studying different aspects of C biogeochemistry of these two estuarine systems during post-monsoon with relatively better spatial coverage compared to previous studies. The post-monsoon sampling was chosen as it identifies as season for peak mangrove leaf litter fall (Ray et al., 2011) that may have positive or negative feedback on estuarine C biogeochemistry as well as relatively stable estuarine condition for spatial sampling. The prime interest of the present study was to understand differences in factors controlling C cycling of these two biogeochemically dissimilar ecosystems and their relative role in exchange of CO_2 across water-atmosphere interface vis-à-vis regional climate change perspective. Specifically, the objectives were to (i) investigate factors controlling DIC and DOC dynamics in the region, (ii) sources of POM in these two contrasting systems, and (iii) partial pressure of CO_2 (pCO_2) and its exchange across water-atmosphere interface at the Hooghly-Sundarbans during postmonsoon period.

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2 Materials and methods

2.1 Study area

The present study was carried out in mangrove dominated estuaries of Indian Sundarbans and anthropogenically dominated Hooghly estuary in the northeastern India. Sundarbans (21ºʼ32ʼ and 22ºʼ40ʼN: 88ºʼ05ʼ and 89ºE), inscribed as a UNESCO world heritage site, is the largest mangrove forest in the world situated at the land-ocean boundary of the Ganges - Brahmaputra delta and the Bay of Bengal (BOB). Out of 10,200 km^2 area of Sundarbans, 41% is in India and the rest is in Bangladesh. The Indian part of Sundarbans (or Sundarbans Biosphere Reserve) contains 4200 km^2 of mangrove reserve forest and 1800 km^2 of estuarine waterways along with reclaimed areas. The Sundarbans is crisscrossed by several rivers, such as Muriganga, Saptamukhi, Thakuran, Matla, Bidya, Gosaba and Haribhanga, forming a sprawling archipelago of 102 islands covered with thick mangroves mostly composed of *Avicennia alba*, *Avicennia marina* and *Avicennia officinalis.* The present study was carried out in three major estuaries of Indian Sundarbans (Saptamukhi, Thakuran and Matla; Fig. 1a) with no perennial source of freshwater and limited supply of anthropogenic inputs only during monsoon (Dutta et al., 2015a).

The Hooghly estuary (21°31′-23°20′N and 87°45′- 88°45′E) is the first deltaic offshoot of the Ganges which ultimately mixes with the northern BOB. Before mixing with the BOB, the lower estuarine part divides into two channels, one being main estuarine stream which directly mixes with the BOB and another smaller channel known as Muriganga. The sampling locations in the Hooghly estuary are shown in Fig.1b. For the purpose of discussion, henceforth, both the estuarine systems will be discussed as ‘Hooghly-Sundarbans system’ and the estuaries of Sundarbans will be called ‘Sundarbans’ unless discussed individually.

2.2 Sampling and experimental techniques

During post-monsoon (November, 2016), surface water samples were collected in duplicate at different locations of the Hooghly-Sundarbans system using Niskin bottle (Oceantest equipment; capacity: 5L). A brief description of the on and off field sampling and experimental techniques used during the present study are described below.

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155 ***2.2.1 Sample collection***

156 Water temperature and pH of the collected samples were measured onboard using
157 thermometer and portable pH meter (Orion Star A211) fitted with a Ross type combination
158 electrode calibrated (as described by Frankignoulle and Borges, 2001) on the NBS scale
159 (reproducibility: ±0.005 pH units). For total alkalinity (TAlk), 50 ml of filtered (0.7-µm
160 filters) estuarine water was titrated onboard in a closed cell using 0.1N HCl following
161 potentiometric titration method (Bouillon et al., 2003). Salinity and dissolved oxygen (DO)
162 concentrations were measured onboard following the Mohr-Knudsen and Winkler titration
163 methods, respectively (Grasshoff et al., 1983).

164 For DIC concentrations ([DIC]) and $\delta^{13}C_{DIC}$ measurements, estuarine waters and
165 groundwater samples from nearby regions were collected by gently overfilling glass vials
166 fitted with teflon septa followed by addition of saturated $HgCl_2$ solution to arrest the
167 microbial activity. Pore-water sample from Lothian Island (one of the virgin island of
168 Sundarbans) was also collected for [DIC] and $\delta^{13}C_{DIC}$ measurements. For DOC concentration
169 ([DOC]) measurement, estuarine water samples were filtered *in situ* through pre-combusted
170 Whatman GF/F filters followed by preservation by adding H_3PO_4 (Bouillon et al., 2003). For
171 suspended particulate matter (SPM), water samples were filtered onboard through pre-
172 weighted and pre-combusted Whatman GF/F filters. Collected DIC, DOC and SPM samples
173 were properly preserved at 4^{o}C during transportation to the laboratory. Additionally,
174 micrometeorological parameters associated with water-atmosphere CO_2 exchange flux
175 computation were continuously monitored at 10 m height over the estuary using a portable
176 weather monitor (DAVIS - Vintage Pro2 Plus).

177 ***2.2.2 Laboratory techniques***

178 DIC concentrations were measured using Coulometer (Model: UIC. Inc. CM - 5130;
179 (uncertainty: ±0.8%) while $\delta^{13}C_{DIC}$ were analyzed using Gas Bench attached to a continuous
180 flow mass spectrometer (Thermo Delta V). Values of $\delta^{13}C_{DIC}$ are reported with respect to V-
181 PDB with reproducibility better than ± 0.10‰. DOC concentrations were measured using
182 high-temperature catalytic oxidation analyzer (Shimadzu TOC 5000) and variability in
183 [DOC] for duplicate measurements was around ± 52 µg L^{-1}. For SPM concentrations, filter
184 papers containing SPM were dried in hot air oven at 60^{o}C and final weights were noted. SPM
185 concentrations were calculated based on difference between final and initial weights of the
186 filter paper and volume of water filtered. For measurement of particulate organic carbon

concentrations ([POC]) and its isotopic composition ($\delta^{13}C_{POC}$), a section of SPM containing filter papers were de-carbonated (by HCl fumes) and analyzed using elemental Analyzer attached to the continuous flow mass spectrometer via conflo. $\delta^{13}C_{POC}$ values are reported relative to V-PDB with reproducibility better than ± 0.10‰.

2.2.3 Computation of %DO, CO_2-system and air - water CO_2 flux calculation

%DO and apparent oxygen utilization (AOU) were calculated as follows: %DO = ($[O_2]_{Measured}$ x 100 / $[O_2]_{Equilibrium}$) and AOU = ($[O_2]_{Measured}$ - $[O_2]_{Equilibrium}$); where, $[O_2]_{Equilibrium}$ is the equilibrium DO concentration calculated at *in-situ* temperature and salinity (Weiss, 1970) and $[O_2]_{Measured}$ is the measured DO concentration of estuarine water. pCO_2 (uncertainty: ± 1%) and other associated parameters of the estuarine CO_2 system were calculated by using equations as given by Millero (2013).

CO_2 exchange fluxes (FCO_2 in µmol m^{-2} hr^{-1}) across water-atmosphere boundary of the estuary were calculated as follows: $FCO_2 = k \times K_H^{CO2} \times [pCO_{2\,(water)} - pCO_{2\,(atmosphere)}]$; where, K_H^{CO2} = CO_2 solubility. 'k' represents gas transfer velocity, which is highly variable and remains a matter of debate (Raymond and Cole, 2001). The 'k' during the present study was computed as a function of wind velocity (Liss and Merlivat, 1986). The computation of 'k' based only on wind velocity are known to vary geographically due to variable impacts of fetch limitation and tidal currents (Borges et al., 2004). For the same wind velocity, the parametrization of Liss and Merlivat, (1986) probably provides least 'k' value over other parametrization (Wanninkhof, 1992; Raymond and Cole, 2001; Borges et al., 2004) and therefore, the FCO_2 presented during this study are the conservative estimates. Mean global atmospheric CO_2 mixing ratio in dry air during 2016 (data source: ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_annmean_gl.txt) was corrected for water vapor partial pressure to calculate $pCO_{2(atmosphere)}$. The fraction, "$K_H^{CO2} \times [pCO_{2\,(water)} - pCO_{2\,(atmosphere)}]$" is the departure of free dissolved CO_2 from atmospheric equilibrium that may be termed as "excess CO_2 (ECO_2)" (Zhai et al., 2005).

3 Results

3.1 Environmental parameters

During the present study, water temperature did not show any distinct spatial trend and varied from 28 - 29 °C and 30.5 - 33 °C for the Sundarbans (Table 1) and Hooghly (Table 2),

respectively. Salinity of the estuaries of Sundarbans varied over a narrow range (12.74 - 16.69; Table 1) with minimum at the upper estuarine location throughout. A relatively sharp salinity gradient was noticed at the Hooghly estuary (0.04 - 10.37; Table 2). Surface water DO concentrations were marginally higher in the Sundarbans (6.46 - 7.46 mgL^{-1}) than the Hooghly (5.24-7.40 mgL^{-1}). Both pH and TAlk in the Hooghly estuary (pH: 7.31 to 8.29, TAlk: 1.80 to 2.86 $meqL^{-1}$) showed relatively wider variation compared to the estuaries of Sundarbans (pH: 8.01 to 8.13, TAlk: 2.01 to 2.29 $meqL^{-1}$; Table 1 & 2).

3.2 Variability in DIC, $\delta^{13}C_{DIC}$ and DOC

In the Sundarbans, both [DIC] and $\delta^{13}C_{DIC}$ varied over a relatively narrow range ([DIC] = 1.68 to 1.92 mM, mean: 1.76 ± 0.07 mM; $\delta^{13}C_{DIC}$ = – 5.93 to – 4.29‰, mean: – 5.04 ± 0.58‰) compared to the Hooghly estuary ([DIC] = 1.79 to 2.70 mM, mean: 2.08 ± 0.32 mM; $\delta^{13}C_{DIC}$ = – 8.61 to – 5.57‰, mean: – 6.95 ± 0.90‰; Table 1 & 2). The present [DIC] and $\delta^{13}C_{DIC}$ values for the mangrove dominated estuaries of the Indian Sundarbans were in the range of that reported for the mangrove surrounding Khura and Trang rivers ([DIC]: ~ 0.25 - 2.25 mM, $\delta^{13}C_{DIC}$: ~ 0 to – 20‰; Miyajima et al., 2009) in peninsular Thailand. The values for the Hooghly estuary were comparable with previously reported values by Samanta et al. (2015). Spatially, in the Hooghly, maximum [DIC] and $\delta^{13}C_{DIC}$ was noticed at freshwater (H1-H6) and mixing (H7-H13) zones, respectively. Different estuaries of the Sundarbans showed different trends with Saptamukhi and Thakuran showing maximum and minimum [DIC] at the upper and lower estuarine regions, respectively with reverse trend for $\delta^{13}C_{DIC}$. However, for the Matla, no distinct spatial trend was noticed for both [DIC] and $\delta^{13}C_{DIC}$.

In comparison to the estuarine surface waters, markedly higher [DIC] and depleted $\delta^{13}C_{DIC}$ were observed for the groundwater (Hooghly: [DIC] = 5.66 to 11.76 mM, $\delta^{13}C_{DIC}$ = – 12.66 to – 6.67‰; Sundarbans: [DIC] = 7.52 to 13.59 mM, $\delta^{13}C_{DIC}$ = – 10.56 to – 6.69‰; Table 3) and pore water samples (Sundarbans: [DIC] = 13.43 mM; $\delta^{13}C_{DIC}$ = – 18.05‰; Table 3) collected from the Hooghly-Sundarbans system.

The [DOC] in the Sundarbans varied from 1.85 to 3.78 mgL^{-1} (mean: 2.83 ± 0.59 mgL^{-1}; Table 1) with no distinct spatial variability. In comparison, ~ 40% higher [DOC] was noticed in the Hooghly (2.82 - 7.95 mgL^{-1}; Table 2) reaching peak in the mixing zone. The [DOC] measured in the Hooghly-Sundarbans system were in the range of that reported for the Godavari estuary, South India (~1 - 8.50 mgL^{-1}; Bouillon et al., 2003) but higher than that reported for the Pearl river estuary, China (~ 0.72 - 1.92 mgL^{-1}; Callahan et al., 2004).

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3.3 Variability in particulate matter and $\delta^{13}C_{POC}$

In the Sundarbans, both SPM and [POC] varied over a wide range (SPM = 80 to 741 mgL^{-1}, mean: 241 ± 197 mgL^{-1}; [POC] = 80 to 436 µM, mean: 173 ± 111 µM; Table 1) with no distinct spatial variability. Compared to that, SPM and [POC] in the Hooghly were relatively lower and varied from 38 - 289 mgL^{-1} and 95 - 313 µM (Table 2), respectively; reaching maximum at the freshwater zone. The $\delta^{13}C_{POC}$ of the Sundarbans varied from –23.82 to –22.85‰ (mean: –23.36 ± 0.32‰); $\delta^{13}C_{POC}$ of the Hooghly, however, was relatively depleted in ^{13}C (–25.95 to –24.07‰, mean: –24.87 ± 0.89‰). The observed $\delta^{13}C_{POC}$ of the Sundarbans were within the range of that reported for mangrove dominated Godavari estuary, South India ($\delta^{13}C_{POC}$: ~ –19 to –29‰, Bouillon et al., 2003) and Khura and Trang rivers, Thailand ($\delta^{13}C_{POC}$ ~ –21 to – 33‰; Miyajima et al., 2009). For the Hooghly, the observed $\delta^{13}C_{POC}$ were comparable with that previously reported by Samanta et al. (2015).

3.4 Variability in pCO_2 and FCO_2

In the Sundarbans, surface water pCO_2 varied from 376 to 561 µatm (mean: 464 ± 66 µatm; Table 1) with no spatial pattern. Compared to the Sundarbans, ~ 3.8 times higher pCO_2 was estimated in the Hooghly estuary (267 – 4678 µatm; Table 2) reaching its peak in the freshwater region. The estimated pCO_2 for the Hooghly-Sundarbans system were in the range of that previously reported for other tidal estuaries of the Indian subcontinent (Cochin estuary: 150-3800 µatm, Gupta et al., 2009; Mandovi - Zuari estuary: 500-3500 µatm, Sarma et al., 2001) and other tropical countries (Changjiang estuary, China: 200-4600 µatm, Zhai et al., 2007).

Except one location at the Sundarbans (M2: – 42 µM) and two mixing zone locations at the Hooghly (H12: –3.26 µM; H13: –3.43 µM), ECO_2 values were always positive at the Hooghly-Sundarbans system. The calculated FCO_2 at the Hooghly estuary (–19.3 to 717.5 $\mu molm^{-2}hr^{-1}$; mean: 231 $\mu molm^{-2}hr^{-1}$; Table 2) was ~17 times higher than the mangrove dominated estuaries of the Indian Sundarbans (–2.6 to 30.3 $\mu molm^{-2}hr^{-1}$; Table 1). Spatially, in the Hooghly, higher FCO_2 was noticed at the freshwater region (285.2 to 717.5 $\mu molm^{-2}hr^{-1}$), while no such distinct spatial trend was noticed at the Sundarbans.

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4 Discussion

4.1 Environmental parameters of the Hooghly-Sundarbans system

Based on the observed salinity gradient, the Hooghly estuary can be divided into two major salinity regimes: (a) fresh-water zone (H1-H6) and (b) mixing zone (H7 – H13; Fig.1b). Due to narrow salinity range, no such classification was possible for the estuaries of Sundarbans. %DO calculations showed relatively well-oxygenated estuarine environment in the Sundarbans (91 - 104%) compared to the Hooghly (71 - 104%; Fig.2a). Salinity independent variation in pH was noticed for both the estuarine systems ($p = 0.14$ and 0.07 for the Sundarbans and Hooghly, respectively; Fig.2b). The pH range for this tropical estuarine system clearly indicates the dominance of [HCO_3^{2-}] over [CO_3^{2-}] in both the Hooghly (~ 8.0 - 219.4 times) and Sundarbans (~ 9.7 - 13.6 times).

4.2 Dissolved inorganic carbon dynamics

In the Hooghly, both [DIC]-salinity ($R^2 = 0.43$, $p = 0.015$) and $\delta^{13}C_{DIC}$ – salinity ($R^2 = 0.58$, $p = 0.003$) relationships were statistically significant (Fig. 3a), making it an ideal site for application of two end member mixing model (Ghosh et al., 2013, Samanta et al., 2015). For model calculation, average salinity, [DIC] and $\delta^{13}C_{DIC}$ of samples collected at ≤ 0.3 salinity during the present study were considered as values for freshwater end member, whereas respective values for marine end member were taken from Dutta et al. (2010) and Akhand et al. (2012). The [DIC] and $\delta^{13}C_{DIC}$ under conservative mixing condition and deviations (ΔDIC and $\Delta\delta^{13}C_{DIC}$) between observed and respective conservative mixing values were computed using Alling et al. (2012) to explore the role of *in situ* biogeochemical processes in modulating estuarine DIC dynamics.

Deviation plot (ΔDIC vs. $\Delta\delta^{13}C_{DIC}$; Fig.3b) for samples of the Hooghly shows following patterns: (a) decrease in ΔDIC with increasing $\Delta\delta^{13}C_{DIC}$ ($n = 5$) indicating phytoplankton productivity and/or outgassing of CO_2 from water-atmosphere interface, (b) decrease in ΔDIC with decreasing $\Delta\delta^{13}C_{DIC}$ ($n = 4$) indicating calcite precipitation, and [c] increase of ΔDIC with increasing $\Delta\delta^{13}C_{DIC}$ ($n = 4$) representing calcite dissolution within the system. Based on these calculations, both organic and inorganic C metabolisms (productivity, $CaCO_3$ precipitation and dissolution) along with physical processes (CO_2 outgassing across water-atmosphere interface) appear to regulate the DIC chemistry in the Hooghly estuary. Spatially, productivity/ CO_2 outgassing appears to be dominant process in the mixing zone as

most of the samples (5 out of 7) from this zone fall in this quadrant, whereas $CaCO_3$ precipitation and/or dissolution are dominant in the freshwater zone (Fig. 3b). Further, 'ΔTAlk/ΔDIC' can be used as a proxy to evaluate relative importance of biological productivity and CO_2 outgassing in the system. For primary productivity ($106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4 \rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2$), theoretical ΔTAlk/ΔDIC is around – 0.16 (ΔTAlk = –17 and ΔDIC = 106, Cao et al., 2011), whereas the same is 0 for CO_2 outgassing as it affects DIC without affecting TAlk (Guo et al., 2008). The ΔTAlk/ΔDIC value for the sampling points located in the productivity/CO_2 outgassing quadrant is –0.17, close to theoretically calculated value for primary productivity. This suggest that primary productivity is the central process regulating DIC chemistry in the mixing zone of the Hooghly estuary.

In the Sundarbans, [DIC] - salinity relationship was not significant ($p = 0.18$), whereas $\delta^{13}C_{DIC}$ - salinity was found to be significant ($R^2 = 0.55$, $p = 0.009$; Fig. 3c) as observed at other mangrove dominated systems as well (Miyajima et al., 2009). Unlike Hooghly, the narrow salinity gradient limits the application of two end member mixing model for the Sundarbans to point out individual influencing biogeochemical factors on DIC. However, the role of mangrove derived OC mineralization becomes important in regulating DIC chemistry in ecosystems like the Sundarbans. Two different mass balance equations as proposed by Miyajima et al. (2009) have been adopted to quantify mangrove derived DIC ($\Delta DIC_{Mangrove}$) in the Sundarbans:

$$\Delta DIC_{Mangrove}\ (\Delta DIC_{M1}) = [DIC] - [DIC_{CM}]$$

$$\Delta DIC_{Mangrove}\ (\Delta DIC_{M2}) = \frac{[DIC] \times [\delta^{13}C_{DIC(CM)} - \delta^{13}C_{DIC}]}{\delta^{13}C_{DIC(CM)} - \delta^{13}C_{Mangrove}\ (= -27‰)}$$

Where, CM indicates conservative mixing. Since both Sundarbans and Hooghly estuarine system have same marine end member (BOB) and the Sundarbans are connected to the Hooghly estuary through different branches, similar end member values as Hooghly were used for this calculation as well. Theoretically, $\Delta DIC_{Mangrove}$ estimated based on [DIC] (ΔDIC_{M1}) and $\delta^{13}C_{DIC}$ (ΔDIC_{M2}) should be equal. The negative and unequal values of ΔDIC_{M2} (– 44 to 66 µM) and ΔDIC_{M1} (–188 to 11 µM) indicate large DIC out-flux over influx through mangrove derived OC mineralization in this tropical mangrove system. The removal mechanisms include CO_2 outgassing across estuarine water-atmosphere boundary

(see section 4.5), phytoplankton uptake and export to adjacent continental shelf region (northern BOB, Ray et al., 2018).

Other than biogeochemical processes, factors such as groundwater and pore-water exchange to the estuary might also play significant role in estuarine DIC chemistry (Tait et al., 2016). High pCO_2, DIC and low pH, TAlk/DIC are general characteristic of groundwater specially within carbonate aquifer region (Cai et al., 2003). Although all the parameters of ground water inorganic C system (like pH, TAlk and pCO_2) were not measured during the present study, groundwater [DIC] were ~5.57 and ~3.61 times higher compared to average surface water [DIC] in the Sundarbans and Hooghly, respectively. The markedly higher [DIC] in groundwater as well as similarity in its isotopic composition with estuarine DIC (Table 3) may stand as a signal for influence of groundwater on estuarine DIC biogeochemistry, with possibly higher influence at the Hooghly rather than Sundarbans as evident from TAlk/DIC value (Hooghly: 0.87-1.14, Sundarbans: 1.12-1.34; Fig.3d). However, unavailability of any data on groundwater discharge rate from these systems limits us to quantitatively evaluate groundwater mediated DIC flux to the estuary. Pore-water [DIC] in the Sundarbans was ~7.63 times higher than the estuarine water indicating possibility of DIC input from the adjoining mangrove system to the estuary through pore-water exchange depending upon changes in hypsometric gradient during tidal fluctuation. Although pore water [DIC] was estimated at only one location, considering postmonsoon pore-water specific discharge and porosity as 0.008 cm min^{-1} and 0.58 (Dutta et al., 2013, Dutta et al., 2015a), respectively, a first-time baseline value for advective DIC influx from mangrove sediment to the estuary can be estimated as ~ 774 mmol m^{-2} d^{-1} using Reay et al. (1995). However, significant impact of pore-water to estuarine DIC may be limited only in mangrove creek water (samples not collected) as evident from narrow variability of estuarine TAlk and DIC as well as no significant correlation between them (Fig. 3d). A comprehensive investigation on ground and pore waters are needed to thoroughly understand their importance in controlling DIC chemistry of the Hooghly-Sundarbans system.

4.3 Dissolved organic carbon dynamics

In estuarine ecosystems, sources of DOC include terrestrial or lateral inputs, *in situ* production by benthic and pelagic primary producers, bacteria, ciliates, flagellates as well as release from zoo-plankton faeces and dead organisms (Wangersky, 1978). During the present study, no significant correlation was found between [DOC] and salinity (Sundarbans: p =

0.10; Hooghly estuary: p = 0.30; Fig.3e) indicating its non-conservative behavior in the Hooghly-Sundarbans system. Similar non-conservative behavior of DOC has been observed in other estuaries of the Indian Subcontinent (Bouillon et al., 2003) with opposite reports from elsewhere as well (Raymond and Bauer, 2001a, Abril et al., 2002). In the Hooghly-Sundarbans system, [DIC] – [DOC] correlation was not significant (Sundarbans: p = 0.29, Hooghly: p = 0.16) suggesting limited role of phytoplankton production on the estuarine DOC level. In contrast to the Hooghly (p = 0.56), significant positive correlation between pCO_2 and [DOC] was observed in the Sundarbans (p = 0.02, n = 11) suggesting analogous sources of pCO_2 and DOC within the system, possibly through pore-water exchange from adjacent mangroves to the estuary as reported from other mangrove systems worldwide (Cai et al., 1999, Ho et al., 2017).

DOC may be removed from system through mineralization by bacteria, oxidation by UV irradiation (photo-oxidation), conversion to POC by flocculation (Bouillon et al., 2006), or export. Considering equal effect of UV mediated DOC photo-oxidation at both estuarine systems, removal of DOC would be principally regulated by biogeochemical and physical processes. The [DOC]-[POC] correlation was found to be significant in the Hooghly (p = 0.04, n = 12) but not at the estuaries of Sundarbans, possibly indicating interconversion between POC and DOC (via dissolving and flocculation, respectively) to be a significant player in controlling DOC levels in the Hooghly. No evidence for significant DOC mineralization was found at the Hooghly - Sundarbans system based on [DOC] – [DO] (Sundarbans: p = 0.85, Hooghly: p = 0.40) as well as pCO_2-[DOC] relationships (described earlier). We do not have data to support export of DOC; however, a recent study quantified an annual export of 0.11-0.34 Tg C and 3.03 Tg C as DOC to the northern BOB from the Hooghly and Sundarbans, respectively (Ray et al., 2018).

4.4 Particulate organic matter in the Hooghly – Sundarbans system

No significant correlation was found between SPM concentrations and salinity for both the estuaries (Sundarbans: p = 0.69, Hooghly: p = 0.40; Fig. not shown). However, [POC] was negatively correlated with salinity in the Hooghly (R^2 = 0.38, p = 0.026; Fig.4a) but not at the Sundarbans (Fig. 4b), indicating freshwater run-off mediated addition of POC in the Hooghly estuary. Additionally, compared to other sampling locations relatively higher [POC] at ‘H1’, ‘H3’ and ‘H4’ at the Hooghly indicate contribution from nearby jute industry located on both sides of river bank at these locations. The POC formed relatively larger part of SPM in the

Hooghly (0.96 - 4.22%; Fig.4a) compared to the Sundarbans (0.66 - 1.23%) (Fig.4b). The lower contribution of POC to the SPM pool in the mangrove dominated Sundarbans may be due to low primary production owing to high SPM load (Ittekkot and Laane, 1991) as observed at mangrove region of the Godavari estuary as well (Bouillon et al., 2003). Although direct measurement of primary productivity was not carried out during the present study, absence of significant correlation between pCO_2 - %DO indirectly points to that effect (Fig. not shown).

Wide range for $\delta^{13}C_{POC}$ (rivers ~ –25 to –28‰; marine plankton ~ –18 to –22‰; C_3 plant ~ –23 to –34‰; C_4 plants ~ –9 to –17‰) have been reported by several researchers in different environments (Hedges et al., 1997, Bouillon et al., 2002, Zhang et al., 1997, Smith and Epstein, 1971, Dehairs et al., 2000). On an average, $\delta^{13}C_{POC}$ at the Hooghly (– 24.87 ± 0.89‰) was relatively lower compared to that of Sundarbans (−23.36 ± 0.32‰) suggesting relatively higher influence of terrestrial inputs in the Hooghly. In the mixing zone of the Hooghly, significantly lower $\delta^{13}C_{POC}$ at 'H11' and 'H12' compared to other locations may be attributed to localized ^{13}C depleted OC influx to estuary from adjacent mangroves and anthropogenic discharge, respectively. No significant correlation between $\delta^{13}C_{POC}$ and salinity (Fig. 4c) was observed during the study period.

Despite being mangrove dominated region, relatively higher $\delta^{13}C_{POC}$ in the Sundarbans compared to mangroves ($\delta^{13}C$ ~ –27‰; Miyajima et al., 2009) suggest marine influence or biogeochemical modification of POC within the estuarine system. Being well-oxygenated system, *in situ* aerobic biogeochemical transformation of POC is very likely to occur within the estuary; however, evidence for *in situ* aerobic POC mineralization was not obvious from the data as relationship between [POC]-pCO_2 was not significant (Fig. not shown). Similar to open ocean environment, the possibility of OC metabolism within isolated anoxic microhabitats of sinking particulate OM exists in the mangrove dominated estuaries of the Indian Sundarbans (Reeburgh et al., 2007), which may favour production of trace gases, such as CH_4. Although CH_4 super-saturation (%CH_4: 2483 ± 50 to 3525 ± 1054) as well as impact of SPM load on CH_4 oxidation have been reported in this oxygenated mangrove environment (Biswas et al., 2007; Dutta et al., 2015a; Dutta et al., 2017), but impact of SPM (or POC) to estuarine CH_4 production as an evidence for *in situ* anaerobic POC modification is not known in the Sundarbans. Our data were also not sufficient to establish *in situ* anaerobic POC metabolism in this oxygenated mangrove environment which demands comprehensive investigation on the fate of POC.

447 In both the estuarine systems, DOC was major constituent of TOC (= DOC + POC)
448 with marginal variability between the Hooghly (43.74-82.05%; mean: 66.17%) and the
449 Sundarbans (33.40-77.26%; mean: 60.06%). Also, dominance of inorganic C was noticed
450 over the organic one throughout the Hooghly-Sundarbans system (TOC/DIC: Sundarbans:
451 0.16 - 0.38, Hooghly: 0.19 - 0.44).
452
453 ***4.5 Exchange flux of CO_2 in the Hooghly-Sundarbans System***
454
455 In the Sundarbans, absence of significant correlation between pCO_2 - salinity and pCO_2-AOU
456 (Fig. 5a and 5b) indicates mostly exogenous CO_2 in the estuarine waters. Our interpretation
457 was also supported by insignificant mangrove derived OM respiration as described in the
458 DIC section earlier (section 4.2) as well as positive pCO_2 – [DOC] relationship (section 4.3).
459 The primary source of exogenous CO_2 in the Sundarbans may be CO_2 influx to the estuarine
460 water from mangrove sediment pore-water exchange during tidal pumping. Although this
461 component was not measured during the present study, it has been reported to be a source of
462 CO_2 in a similar estuarine-intertidal marsh complex of five rivers in the southeastern USA
463 (Cai et al., 1999). In the Hooghly, significant negative and positive relationships between
464 pCO_2-salinity ($R^2 = 0.58$, $p = 0.002$; Fig 5a) and pCO_2 - AOU ($R^2 = 0.37$, $p = 0.028$; Fig 5b)
465 provide evidences for both freshwater run-off and *in situ* aerobic OC mineralization mediated
466 influx of CO_2 in the system. The significant impact of aerobic OC mineralization on estuarine
467 pCO_2 levels have been observed in other tropical estuarine systems (Zhai et al., 2005; Dai et
468 al., 2006). Significant OC mineralization mediated CO_2 addition coupled with its
469 insignificant impact on [DIC] and $\delta^{13}C_{DIC}$ in the Hooghly estuary (see section 4.2) might
470 suggest substantial outgassing or export of CO_2 from the system. Using average AOU values
471 and stoichiometric equation of OC respiration [$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow 106CO_2$
472 $+ 16HNO_3 + H_3PO_4 + 122H_2O$], approximate CO_2 generation through OC mineralization (or
473 respiration) at any instant in the Hooghly estuary was estimated around ~ 21.02 $\mu molCO_2\ L^{-1}$.
474 For both the estuaries, positive mean FCO_2 clearly suggest the Hooghly-Sundarbans
475 system to be a net source of CO_2 to the regional atmosphere during postmonsoon (Fig.5c).
476 Specifically, from regional climate and environmental change perspective, anthropogenically
477 influenced Hooghly estuary was a relatively greater source of CO_2 to the regional atmosphere
478 compared to the mangrove dominated Sundarbans as evident from significantly higher CO_2
479 emission flux from the Hooghly ($[FCO_2]_{Hooghly}$: $[FCO_2]_{Sundarbans} = 17$). FCO_2 measured for the
480 estuaries of Sundarbans was markedly higher than global mean FCO_2 (~63 $\mu molm^{-2}d^{-1}$)

observed in mangrove creek and other similar estuaries (Call et al., 2015). However, FCO_2 measured for the Hooghly estuary was relatively lower compared to some Chinese estuarine systems (Pearl River inner estuary: 46 mmol m^{-2} d^{-1}, Guo et al., 2009; Yangtze River estuary: 41 mmol m^{-2} d^{-1}, Zhai et al., 2007). The inter-estuary variability of FCO_2 may be due to variability in pCO_2 level as well as micrometeorological and physicochemical parameters controlling gas transfer velocity across water-atmosphere interface. Taken together, it appears that difference in land use and degree of anthropogenic influence have the potential to alter the C biogeochemistry of aquatic ecosystems with anthropogenically stressed aquatic systems acting as a relatively bigger source of CO_2 to the regional atmosphere.

Conclusions

The present study focused on investigating different aspects of C biogeochemistry of the anthropogenically affected Hooghly estuary and mangrove dominated estuaries of the Sundarbans during postmonsoon. Following conclusions were deduced from the study:

- With the exception of SPM, physicochemical parameters of the Hooghly estuary varied over a relatively wider range compared to the Sundarbans.
- Phytoplankton productivity was a major controlling factor on DIC in the mixing zone of the Hooghly with carbonate precipitation and dissolution being dominant in the freshwater regime. In the Sundarbans, signal for mangrove derived DIC removal was noticed.
- DOC behaved non-conservatively in the Hooghly-Sundarbans system. Evidence for DOC to POC interconversion was observed in the Hooghly. Analogous sources of pCO_2 and DOC in the form of pore-water exchange was found in the Sundarbans.
- In the Sundarbans, contribution of terrestrial organic matter to the POM pool was relatively lower compared to the Hooghly with possibility of *in situ* biogeochemical modifications in the Sundarbans.
- During postmonsoon, the entire Hooghly-Sundarbans system acted as a source of CO_2 to the regional atmosphere. In the Hooghly estuary, CO_2 is added through freshwater runoff and OC mineralization, whereas CO_2 in the Sundarbans is principally exogenous.

Data availability

Data used in the manuscript is presented in tables (Table 1, Table 2, and Table 3) of the manuscript.

Author contributions

MKD and SK designed the study. MKD with RM and PS collected and analyzed samples. MKD and SK interpreted the data and drafted the manuscript. SKM provided facility to measure basic physicochemical parameters and DOC.

Competing interest

The author declares no conflict of interest.

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Figure Captions:

Fig. 1: Sampling locations at the (a) estuaries of Sundarbans, and (b) Hooghly estuary.

Fig. 2: Variability of (a) %DO, and (b) pH with salinity at the Hooghly-Sundarbans systems.

Fig. 3: (a) Observed and conservative mixing values of [DIC] and $\delta^{13}C_{DIC}$ with salinity at the Hooghly estuary, [b] ΔDIC and Δ $\delta^{13}C_{DIC}$ at the Hooghly estuary (PP = Phytoplankton productivity, CD = carbonate dissolution, CP = carbonate precipitation, ROM = Respiration of organic matter), (c) [DIC] and $\delta^{13}C_{DIC}$ with salinity at the estuaries of Sundarbans, [d] TAlk and [DIC], and (e) [DOC] with salinity in the Hooghly-Sundarbans system.

Fig.4: Variability of (a) [POC] and %POC/SPM with salinity in the Hooghly, (b) [POC] and %POC/SPM with salinity in the Sundarbans, and (c) $\delta^{13}C_{POC}$ in the Hooghly – Sundarbans system with salinity.

Fig.5: Variability in (a) pCO_2 with salinity, (b) pCO_2 with AOU, and [c] FCO_2 with salinity in the Hooghly-Sundarbans system.

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845 Table - 1: Physicochemical parameters, inorganic and organic C related parameters, and CO_2
846 exchange fluxes across water-atmosphere at the estuaries of Sundarbans. Here, water
847 temperature (W_T), DO, isotopic compositions, DIC, DOC, POC, pCO_2 and FCO_2 are
848 presented in '^oC' 'mgL^{-1}', '‰', 'mM', 'mgL^{-1}', 'µM', 'µatm' and 'µmol m^{-2} hr^{1}',
849 respectively.

Station	W_T	Salinity	DO	pH	DIC	$\delta^{13}C_{DIC}$	DOC	POC	$\delta^{13}C_{POC}$	pCO_2	FCO_2
S1	28.50	12.74	6.65	8.02	1.78	– 5.59	3.34	154	– 22.85	536	26.5
S2	28.00	16.02	6.65	8.02	1.70	– 4.33	3.20	124	– 23.54	561	30.3
S3	28.00	16.69	6.61	8.12	1.70	– 4.29	2.36	114	– 23.43	395	0.9
S4	29.00	15.25	6.46	8.01	1.86	– 5.27	3.78	93	– 23.68	543	27.6
T1	29.00	14.30	6.56	8.05	1.76	– 5.57	3.11	80	– 23.62	490	18.1
T2	29.00	15.51	6.74	8.07	1.73	– 4.79	2.19	106	– 23.21	456	11.9
T3	28.50	16.55	6.46	8.11	1.68	– 4.39	1.85	154	– 22.97	403	2.4
M1	28.00	15.14	6.99	8.07	1.71	– 5.93	3.38	264	– 23.07	443	9.4
M2	28.00	15.14	6.91	8.12	1.74	– 4.63	2.62	436	– 23.15	376	-2.6
M3	28.00	15.23	7.46	8.13	1.74	– 5.30	2.66	287	– 23.62	401	1.9
M4	28.50	14.78	6.84	8.04	1.92	– 5.38	2.58	96	– 23.82	503	20.3

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851 Table - 2: Physicochemical parameters, inorganic and organic C related parameters, and CO_2
852 exchange fluxes across water-atmosphere at the Hooghly estuary. Here, water temperature
853 (W_T), DO, all isotopic compositions, DIC, DOC, POC, pCO_2 and FCO_2 are presented in '^oC'
854 'mgL^{-1}', '‰', 'mM', 'mgL^{-1}', 'µM', 'µatm' and 'µmol m^{-2} hr^{1}', respectively.

Station	W_T	Salinity	DO	pH	DIC	$\delta^{13}C_{DIC}$	DOC	POC	$\delta^{13}C_{POC}$	pCO_2	FCO_2
H1	32.0	0.04	6.29	7.92	2.70	– 6.98	2.92	313	– 25.34	2036	285.2
H2	33.0	0.07	6.11	7.71	1.68	– 8.38	3.65	177	– 25.19	2316	343.8
H3	31.0	0.08	6.45	7.83	2.50	– 6.70	2.82	286	– 25.95	2490	355.4
H4	31.0	0.13	5.24	7.73	2.45	– 7.38	2.91	254	– 25.40	2691	389.2
H5	31.0	0.19	5.38	7.77	2.36	– 7.56	4.08	130	– 25.67	2123	293.1
H6	30.5	0.32	5.66	7.31	2.16	– 8.61	3.70	116	– 24.07	4678	717.5
H7	31.5	5.83	6.71	7.68	1.83	– 6.79	7.95	145	– 24.70	1184	132.0
H8	31.0	5.19	7.14	7.31	2.02	– 6.78	4.25	139	– 23.47	3153	455.8
H9	31.5	9.08	6.62	7.90	1.92	– 6.08	3.98	161	– 23.53	665	44.9
H10	31.5	9.72	6.17	8.08	1.79	– 5.78	2.99	95	– 24.06	452	10.1
H11	31.0	8.43	6.37	8.07	1.98	– 7.21	4.29	95	– 25.94	486	15.6
H12	31.5	5.83	7.40	8.29	1.87	– 6.60	3.12	133	– 26.28	274	-19.3
H13	31.0	10.37	7.00	8.24	1.84	– 5.57	4.72	129	– 24.72	267	-19.8

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863 Table - 3: The [DIC] and $\delta^{13}C_{DIC}$ of groundwater (GW) and pore-water (PW) samples
864 collected from the Hooghly-Sundarbans system.

Ecosystem	Station	[DIC] (mM)	$\delta^{13}C_{DIC}$ (‰)
Hooghly	H3GW	11.76	– 12.66
	H4GW	6.23	– 7.85
	H5GW	6.33	– 8.96
	H6GW	7.03	– 11.27
	H7GW	5.66	– 6.91
	H11GW	9.12	– 7.67
	H12GW	6.86	– 7.49
	H13GW	7.26	– 7.21
	Gangasagar GW	7.25	– 6.67
Sundarbans	Lothian GW	7.52	– 6.84
	Lothian PW	13.43	– 18.05
	Kalash GW	13.59	– 6.69
	Virat Bazar GW	8.30	– 10.56

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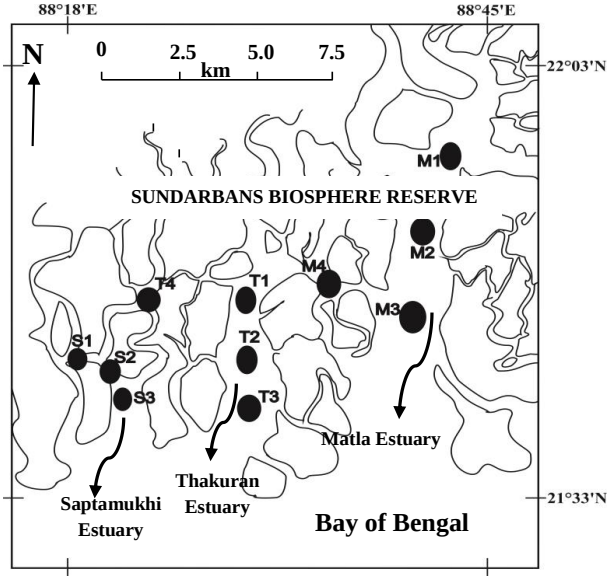

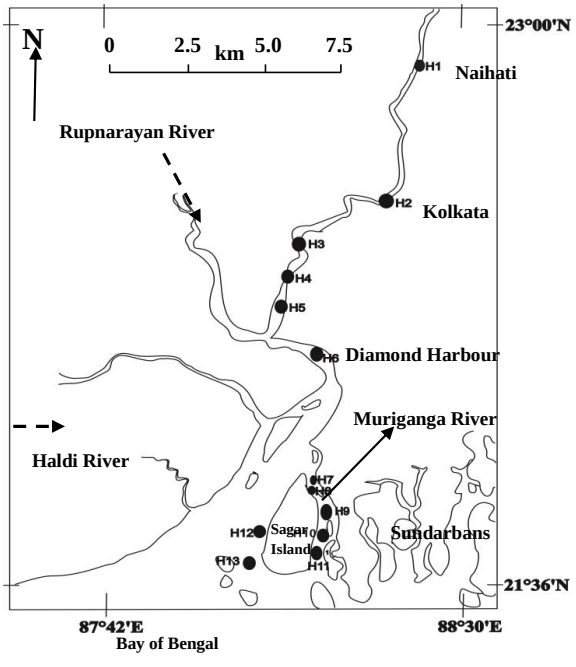

Fig. 1

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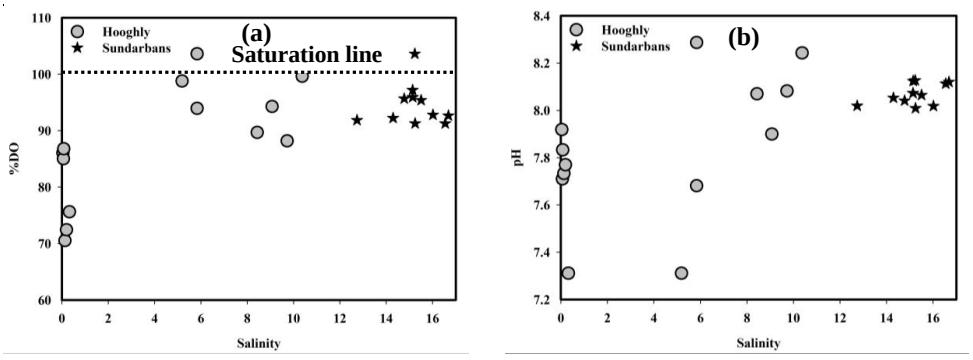

Fig. 2

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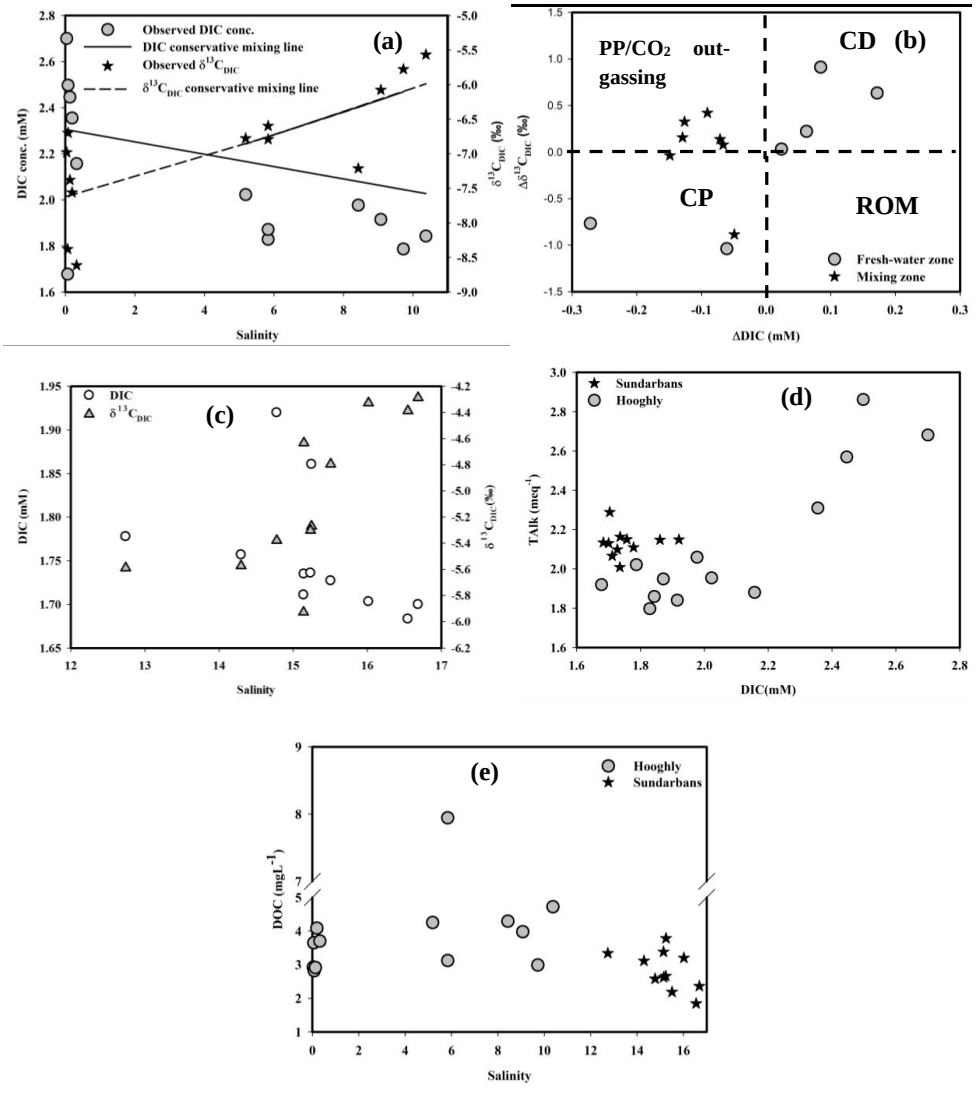

Fig. 3

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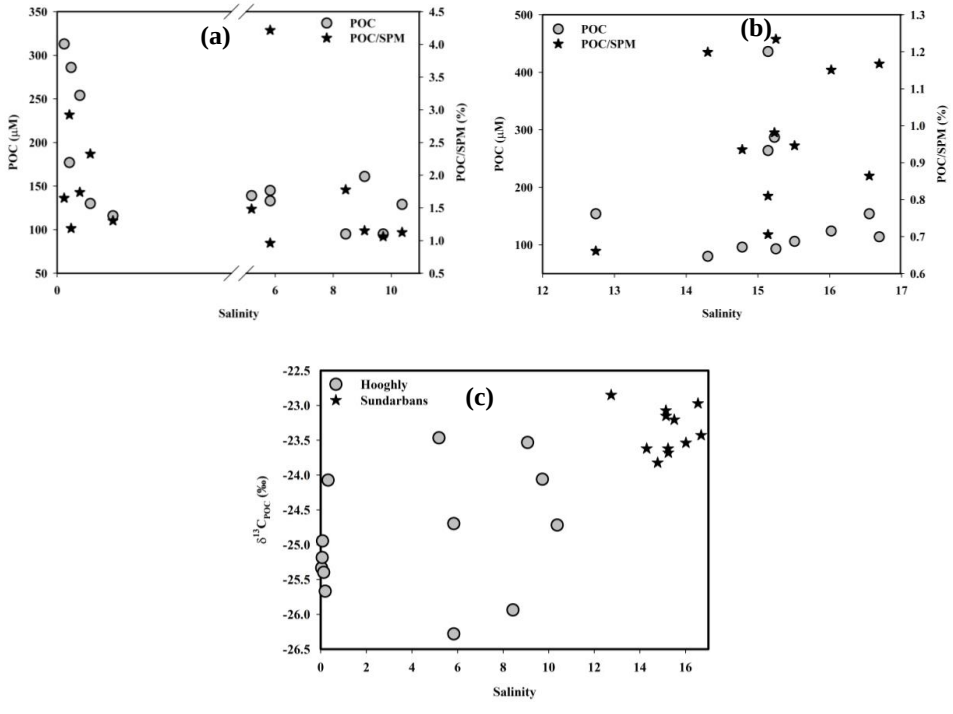

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906 **Fig. 4**

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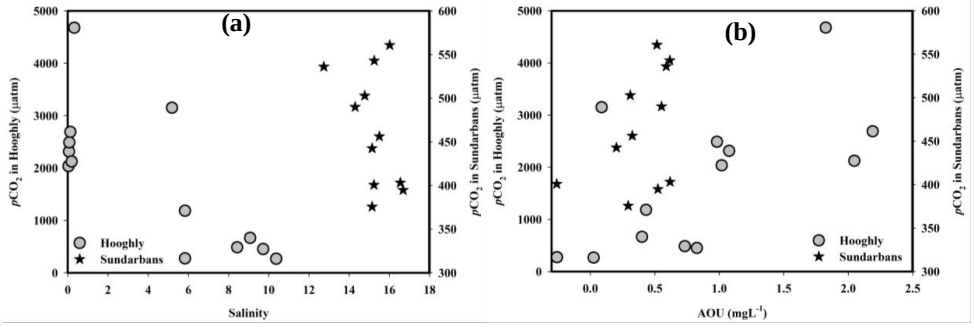

Fig. 5