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

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Abstract

The present study focused on understanding differences in postmonsoon carbon (C) biogeochemistry of two adjacent estuaries undergoing different levels of anthropogenic stress by investigating anthropogenically influenced Hooghly estuary and mangrove-dominated estuaries of the Sundarbans in the north-eastern India. The salinity of well oxygenated (%DO: 91 - 104%) estuaries of the Sundarbans varied over a narrow range (12.74 - 16.69) relative to the Hooghly (0.04 - 10.37). Apart from freshwater contribution, mixing model suggested carbonate precipitation and dissolution to be major processes controlling DIC in the in the freshwater region of the Hooghly, whereas phytoplankton productivity and CO_2 outgassing dominated mixing zone. The signatures of significant DIC removal over addition through mangrove derived organic C mineralization was observed in the Sundarbans. The DOC in the Hooghly was ~ 40% higher compared to the Sundarbans, which was largely due to cumulative effect of anthropogenic inputs, biogeochemical processes and groundwater contribution rather than freshwater mediated inputs. The measured $\delta^{13}C_{POC}$ in the Hooghly suggested organic matter contributions from different sources (freshwater runoff, terrestrial C_3 plants and anthropogenic discharge), whereas evidence for only C_3 plants was noticed at the Sundarbans. The significant departure of $\delta^{13}C_{POC}$ from typical mangrove $\delta^{13}C$ in the mangrove-dominated Sundarbans suggested significant POC modifications. The average pCO$_2$ in the Hooghly was ~ 1291 µatm higher compared to the Sundarbans with surface run-off and organic matter respiration as dominant factors controlling pCO$_2$ in the Hooghly and Sundarbans, respectively. 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. Taken together, the cycling of C in estuaries with different levels of anthropogenic influences are clearly different with dominance of anthropogenically influenced estuary over relatively pristine mangrove-dominated one as CO_2 source to the regional atmosphere.

1 Introduction

Situated at the interface of land and sea, estuaries are highly susceptible to anthropogenic inputs and undergo intricate biogeochemical and hydrological processes. 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. Tropical rivers, which constitute ~ 66% of global river water discharge, deliver ~ 0.53Pg C to the estuaries annually (Huang et al., 2012). The majority of this exported C is in dissolved form [dissolved inorganic C (DIC): 0.21PgCyr^{-1} and dissolved organic C (DOC): 0.14PgCyr^{-1}] with some contribution as particulate [particulate organic C (POC): 0.13PgCyr^{-1} and particulate inorganic C (PIC): 0.05PgCyr^{-1}] (Huang et al., 2012). 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, albeit with large uncertainty (Borges et al., 2005; Chen and Borges, 2009; Cai et al., 2006; Cai, 2011). This suggests estuaries to be not only active pathway for transport of C (Ittekkot and Laane, 1991) but also a hotspot for biogeochemical modification of labile 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 ± 72Tg C yr^{-1} (Bouillon et al. 2008). Fine root production coupled with litter fall and wood production are primary sources of mangrove derived C to intertidal sediment (Bouillon et al., 2008). The fate of this mangrove derived C remains poorly understood. Despite taking C burial and CO_2 emission flux across mangrove sediment-atmosphere interface into account, estimates of global mangrove C budget revealed a significant imbalance (~72%) between mangrove net primary productivity and its sinks (Bouillon et al., 2008). Earlier studies reported mangroves to be responsible for ~10% of the global terrestrial derived POC and DOC export to the coastal zones (Jennerjahn and Ittekkot, 2002; Dittmar et al. 2006). However, recent studies proposed DIC exchange as major C export pathway from mangrove forests, which was ~70% of the total mineralized C transport from mangrove forests to coastal waters (Maher et al., 2013; Alongi, 2014; Alongi and Mukhopadhyay, 2014). Another study reported groundwater advection from mangrove to be responsible for 93-99% of total DIC export and 89-92% of total DOC export to the coastal ocean (Maher et al., 2013). Upon extrapolating these C export fluxes to the global mangrove area, it was found that the calculated C exports were similar to the missing mangrove C sink (Sippo et al., 2016). The remaining C that escapes export gets buried in sub-surface sediment layers and participates in anaerobic processes (linked to production of biogenic trace gases like CH_4) or undergoes 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 regulate 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. The biogeochemical cycling of bioavailable elements, such as C and N, in 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). However, this is not always the case as observed in Guanabara Bay, Brazil, which acts as a strong CO_2 sink enhanced by eutrophication (Cotovicz Jr. et al., 2015). Lack of ample quantitative estimation of above-mentioned biogeochemical processes in many regions of the world restrains biogeochemists from an in-depth understanding of these processes in different ecological settings. It also leads to uncertainty in estimation of C budget of coastal regions 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 (Fig. 1). Characteristically, these two estuaries are very different from each other. The Hooghly estuary experiences significantly higher anthropogenic influence compared to mangrove-dominated Sundarbans as evidenced by high nutrient and freshwater input (Table 1). The anthropogenic influences largely include supply of the industrial effluents and domestic sewage on daily basis from industries and major cities (Kolkata and Howrah) located upstream (Table 1). The industries along the Hooghly is principally *jute* (*Corchorus olitorius*) based industry, which produces fabrics for packaging a wide range of agricultural and industrial commodities.

The major focus of biogeochemical studies in the Hooghly and Sundarbans has been on trace gases (Mukhopadhyay et al., 2002; Biswas et al., 2004, 2007; Ganguly et al., 2008, 2009; Dutta et al., 2013, 2015, 2017) with exception of one comprehensive study on nutrient budget at the Hooghly estuary (Mukhopadhyay et al., 2006). Recently, attempts have been made to understand different aspects of C cycling in these two estuaries by different workers (Samanta et al., 2015; Ray et al., 2015, 2018; Akhand et al., 2016). Samanta et al. (2015) have comprehensively studied DIC dynamics in the Hooghly estuary, whereas Akhand et al. (2016) focused on DIC and pCO_2 at the Hooghly-Matla estuary. Different aspects of C cycling in Hooghly-Sundarbans system have been reported by Ray et al. (2015, 2018). Barring Samanta et al. (2015), which has wider spatial and temporal coverage with respect to DIC in the Hooghly, other studies are severely limited in spatial coverage with focus on mid to lower part of the Hooghly estuary and a few locations in the Sundarbans (one location by Ray et al., 2015, 2018; three locations by Akhand et al., 2016). 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 understanding differences in varied aspects of C cycle (particulate organic, dissolved inorganic and organic along with gaseous form) of the Hooghly and Sundarbans during postmonsoon with relatively better spatial coverage compared to previous studies. The postmonsoon sampling was chosen because of relatively stable estuarine condition for wider spatial coverage and peak mangrove leaf litter fall during this season (Ray et al., 2011), which may have influence on estuarine C dynamics. Considering different nature and quantity of supplied OM within these two contrasting system, we hypothesize C metabolism between these two estuaries to be very different with higher CO_2 exchange flux from anthropogenically influenced estuary compared to mangrove-dominated estuary. Specifically, the major aims of the present study were to: (a) investigate factors controlling DIC and DOC dynamics in the region, (b) sources of POM in these two contrasting systems, and (c) partial pressure of CO_2 (pCO_2) and its controlling mechanisms along with exchange across water-atmosphere interface at the Hooghly-Sundarbans during postmonsoon period.

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 (21^{o}32’ and 22^{o}40’N: 88^{o}05’ and 89^{o}E), 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.* Semidiurnal tide with mean depth ~ 6 m is general characteristic of the estuary (Dutta et al., 2015).

The second study site, 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. Like estuaries of Sundarbans, tides are semidiurnal in nature in the Hooghly as well with variable depth along the channel (~ 21 m at Diamond Harbor (H6) to ~ 8 m at the mouth of the estuary; Fig 1b) (CIFRI, 2012). Before mixing with the BOB, the lower estuarine part of the Hooghly divides into two channels, one being main estuarine stream which directly mixes with the BOB and another smaller channel known as Muriganga (mean depth ~ 6 m; Sadhuram et al., 2005). The width of the river at the mouth of the estuary is ~ 25 km (Mukhopadhyay et al., 2006). Both estuarine systems experience typical tropical climate having three distinct seasons: premonsoon (February - May), monsoon (June - September) and postmonsoon (October - January) with ~ 80% rainfall during monsoon.

Covering upper, middle, and lower estuarine regions, the present study was carried out during low tide condition in three major estuaries of the Indian Sundarbans [Saptamukhi (S1-S3), Thakuran (T1-T3), and Matla (M1-M3); Fig. 1a] along with its related waterways (S4 & M4). The low-tide postmonsoon sampling was preferred as it was ideal time to evaluate the effect of mangroves on the adjoining estuary due to peak mangrove litter fall (Ray et al., 2011) and groundwater (or pore-water) discharge. To compare and bring out the contrast in different components of the C cycle between mangrove-dominated and anthropogenically influenced estuaries, low-tide sampling was also performed at 13 locations (H1 – H13, Fig. 1b) in the Hooghly estuary (stretch: ~150km).

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 postmonsoon (November, 2016), estuarine 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.

2.2.1 Sample collection and on board measurements

Water temperature and pH of the collected samples were measured onboard using thermometer (±0.1°C) and portable pH meter (Orion Star A211) fitted with a Ross type combination electrode calibrated (as described by Frankignoulle and Borges, 2001) on the NBS scale (reproducibility: ±0.005 pH units). Salinity (±0.1) and dissolved oxygen (DO: $\pm 0.1 mgL^{-1}$) concentrations were measured onboard following the Mohr-Knudsen and Winkler titration methods, respectively (Grasshoff et al., 1983). For total alkalinity (TAlk), 50 ml of filtered (Whatman GF/F filter) estuarine water was titrated onboard in a closed cell using 0.1N HCl following potentiometric titration method (Bouillon et al., 2003). Uncertainty in TAlk measurements was ± 1 $\mu molkg^{-1}$ as estimated using certified reference material (Dickson standard: CRM-131-0215).

For DIC and $\delta^{13}C_{DIC}$ measurements, estuarine surface waters were collected by gently overfilling glass vials fitted with teflon septa. Pore-water was also collected from lower littoral zone of the Lothian Island (one of the virgin island of the Indian Sundarbans) by digging a hole (~30 cm below the water table). It was not possible to collect pore-water samples from mid and upper littoral zones due to logistic problems. After purging water at least twice in the bore, sample was collected from the bottom of the bore through syringe and transferred to the glass vial (Maher et al., 2013). Twelve groundwater samples were collected from the nearby locations of the Hooghly-Sundarbans system via tube pump. After collection, all samples for DIC and $\delta^{13}C_{DIC}$ were preserved immediately by adding saturated $HgCl_2$ solution to arrest the microbial activity.

For both DOC and SPM (suspended particulate matter) measurements, surface water samples were filtered on board through pre-weighted and pre-combusted (500°C for 6 hours) Whatman GF/F filters (pore size: 0.7µm). Filtrate was kept for DOC analysis in brown bottles followed by immediate preservation via addition of H_3PO_4 (50µL/15 mL sample) (Bouillon et al., 2003), whereas the residue was kept for particulate matter analysis. Collected DIC, DOC and SPM samples were properly preserved at 4 °C during transportation to the laboratory. Additionally, micrometeorological parameters associated with water-atmosphere CO_2 exchange flux computation were continuously monitored at 10 m height over the estuary using a portable weather monitor (DAVIS - Vintage Pro2 Plus).

2.2.2 Laboratory measurements

The DIC were measured using Coulometer (Model: UIC. Inc. CM – 5130) with analytical uncertainty of ±0.8%. The $\delta^{13}C_{DIC}$ were measured using Gas Bench attached to a continuous flow mass spectrometer (Thermo Delta V) with precision better than 0.10‰. The DOC were measured using high-temperature catalytic oxidation analyzer (Shimadzu TOC 5000), which was calibrated using potassium hydrogen phthalate (KHP) solution containing 1, 2, 5, 10, 20 mg L^{-1} of DOC (Ray et al., 2018). The analytical error for DOC measurement was < 2%. For SPM measurement, filter papers containing SPM were dried in hot air oven at 60°C and final weights were noted. The SPM were calculated based on difference between final and initial weights of the filter paper and volume of water filtered. For measurement of POC and $\delta^{13}C_{POC}$, SPM containing filter papers were de-carbonated (by HCl fumes) and analyzed using Elemental Analyzer attached to the continuous flow mass spectrometer via conflo. The $\delta^{13}C_{POC}$ values are reported relative to V-PDB with reproducibility better than ± 0.10‰, whereas uncertainty for POC was <10%.

2.2.3 Computation of air - water CO_2 flux and %DO

The pCO_2 was calculated based on surface water temperature, salinity, TAlk, pH and dissociation constants calculated following Millero (2013). The uncertainty for estimated pCO_2 was ± 1%. The CO_2 exchange fluxes (FCO_2 in µmol m^{-2} hr^{-1}) across water-atmosphere boundary of the estuary were calculated as follows:

$$FCO_2 = k \text{ x } K_H^{CO2} \text{ x } [pCO_{2\,(water)} - pCO_{2\,(atmosphere)}]$$

Where, K_H^{CO2} = CO_2 solubility. 'k' is 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 following Liss and Merlivat (1986) parametrization. For the same wind velocity, the parametrization of Liss and Merlivat (1986) 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 may be considered as the conservative estimates. The wind velocity based 'k' estimation for the Hooghly-Sundarbans system has been applied in earlier studies as well (Mukhopadhyay et al., 2002, Biswas et al., 2004). 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} x [$pCO_{2\,(water)}$ – $pCO_{2\,(atmosphere)}$]" 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).

%DO and apparent oxygen utilization (AOU) were calculated as follows:

$$\%DO = ([O_2]_{Measured} \times 100 / [O_2]_{Equilibrium})$$

$$AOU = ([O_2]_{Measured} - [O_2]_{Equilibrium})$$

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 surface water.

2.2.4 Mixing model calculation

Considering salinity as a conservative tracer and an ideal indicator for estuarine mixing mechanism (Fry, 2002), conservative mixing model was applied to the Hooghly estuary to understand addition/removal of dissolved and particulate C by *in situ* biogeochemical processes. Concentrations and stable isotopic compositions of dissolved or particulate C (presented as C) during conservative mixing (C_{CM} and $\delta^{13}C_{CM}$) were computed as follows (Carpenter et al., 1975, Mook and Tan, 1991):

$$C_{CM} = C_F F_F + C_M F_M$$

$$\delta^{13}C_{CM} = \frac{S_S\,[C_F\,\delta^{13}C_F - C_M\,\delta^{13}C_M] + S_F\,C_M\,\delta^{13}C_M - S_M\,C_F\,\delta^{13}C_F}{S_S\,(C_F - C_M) + S_F\,C_M - S_M\,C_F}$$

Here, 'S' denotes salinity, the suffixes CM, F, M and S denote conservative mixing, freshwater end member, marine end member and sample, respectively. F_F = freshwater fraction = 1 – (S_S

/ S_M) and F_M = marine water fraction = (1– F_F). $C_{Sample} > C_{CM}$ indicates C addition, whereas reverse indicates removal. For model calculation, mean salinity, concentrations of C and $\delta^{13}C$ of samples collected at salinity ≤ 0.3 at the Hooghly estuary were considered as end member values for freshwater, whereas respective values for marine end member were taken from Dutta et al. (2010) and Akhand et al. (2012). Quantitative deviations (ΔC and $\Delta\delta^{13}C$) of measured C concentrations and $\delta^{13}C$ from the respective conservative mixing values were estimated as follows (Alling et al., 2012):

$$\Delta C = (C_{Sample} - C_{CM}) / C_{CM}$$

$$\Delta\delta^{13}C = \delta^{13}C_{Sample} - \delta^{13}C_{CM}$$

Plots between ΔC and $\Delta\delta^{13}C$ for DIC and POC have been used to understand processes influencing DIC and POC in the Hooghly-Sundarbans system. However, the above model could not be applied to DOC due to unavailability of $\delta^{13}C_{DOC}$ during the present study.

Unlike Hooghly, direct application of above-mentioned conservative mixing model was not justified for mangrove-dominated Sundarbans due to narrow salinity gradient (see later). However, assuming that apart from conservative mixing only mangrove derived C ($\Delta C_{Mangrove}$) contributes to estuarine C pool, an approach can be taken to quantify $\Delta C_{Mangrove}$. Two different mass balance equations as used by Miyajima et al. (2009) for estimating $\Delta DIC_{Mangrove}$ was extended to calculate $\Delta C_{Mangrove}$ during the present study:

$$\Delta C_{Mangrove} (\Delta C_{M1}) = C_{Sample} - C_{CM}$$

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

For model calculation, $\delta^{13}C_{Mangrove}$ was taken as – 28.4‰ for Sundarbans (Ray et al., 2015) and end members were taken as same as the Hooghly as estuaries of Sundarbans are offshoot of lower Hooghly estuary.

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 2) and Hooghly (Table 3), respectively. Salinity of the estuaries of Sundarbans varied over a narrow range (12.74 - 16.69; Table 2) with minimum at the upper estuarine location throughout. A relatively sharp salinity gradient was noticed at the Hooghly estuary (0.04 - 10.37; Table 3). 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: 1797 to 2862 μeqL^{-1}) showed relatively wider variation compared to the estuaries of Sundarbans (pH: 8.01 to 8.13, TAlk: 2009 to 2289 μeqL^{-1}; Table 2 & 3).

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 = 1683 to 1920 µM, mean: 1756 ± 73 µM; $\delta^{13}C_{DIC}$ = – 5.93 to – 4.29‰, mean: – 5.04 ± 0.58‰) compared to the Hooghly estuary (DIC = 1678 to 2700 µM, mean: 2083 ± 320 µM; $\delta^{13}C_{DIC}$ = – 8.61 to – 5.57‰, mean: – 6.95 ± 0.90‰; Table 2 & 3). 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 = 5655 to 11756 µM, $\delta^{13}C_{DIC}$ = – 12.66 to – 6.67‰; Sundarbans: DIC = 7524 to 13599 µM, $\delta^{13}C_{DIC}$ = – 10.56 to – 6.69‰; Table 4) and pore-water samples (Sundarbans: DIC = 13425 µM; $\delta^{13}C_{DIC}$ = – 18.05‰; Table 4) collected from the Hooghly-Sundarbans system. The DOC in the Sundarbans varied from 154 to 315 µM (mean: 235 ± 49 µM; Table 2) with no distinct spatial variability. In comparison, ~ 40% higher DOC was noticed in the Hooghly (235 - 662 µM; Table 3) reaching peak in the mixing zone.

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 2) 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 3), 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‰), whereas in the Hooghly it varied from –26.28 to –24.06 (mean: –24.87 ± 0.89‰).

3.4 Variability in pCO_2 and FCO_2

In the Sundarbans, surface water pCO_2 varied from 376 to 561µatm (mean: 464 ± 66µatm; Table 2) with no spatial pattern. Compared to the Sundarbans, ~ 3.8 times higher pCO_2 was estimated in the Hooghly estuary (267 - 4678µatm; Table 3) reaching its peak in the freshwater region. 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 in the Hooghly-Sundarbans system. The calculated FCO_2 at the Hooghly estuary (–19.8 to 717.5 $\mu mol m^{-2} hr^{-1}$; mean: 231 $\mu mol m^{-2} hr^{-1}$; Table 3) was ~17 times higher than the mangrove dominated estuaries of the Indian Sundarbans (–2.6 to 30.3 $\mu mol m^{-2} hr^{-1}$; Table 2). Spatially, in the Hooghly, higher FCO_2 was noticed at the freshwater region (285.2 to 717.5 $\mu mol m^{-2} hr^{-1}$), while no such distinct spatial trend was noticed at the Sundarbans.

4. Discussion

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. 2). Based on the results obtained during the present study, below we discuss different components of C cycle within Hooghly-Sundarbans system.

4.1 Major drivers of DIC dynamics

In the Hooghly, DIC concentrations during the present study were relatively higher compared to that reported by Samanta et al. (2015) for the same season, whereas $\delta^{13}C_{DIC}$ values were within the same range (DIC: 1700 - 2250µM; $\delta^{13}C_{DIC}$: –11.4 to – 4.0‰). Statistically significant correlations between DIC - salinity (r^2 = 0.43, p = 0.015) and $\delta^{13}C_{DIC}$ - salinity (r^2 = 0.58, p = 0.003) in the Hooghly suggested potential influence of marine and freshwater mixing on DIC and $\delta^{13}C_{DIC}$ in the estuary (Fig. 3a & 3b). The above-mentioned significant relationships during the present study coupled with earlier $\delta^{18}O$ - salinity (Ghosh et al., 2013) and DIC dynamics (Samanta et al., 2015) studies in the Hooghly rationalize application of two end member mixing model in this estuary to decipher *in situ* processes influencing DIC chemistry.

Based on the methodology discussed earlier, calculated ΔC for DIC (ΔDIC ~ – 0.27 to 0.17) predicted dominance of DIC addition (n = 4) over removal (n = 2) in the freshwater region of the Hooghly, whereas only removal was evident in the mixing zone. In case of $\Delta\delta^{13}C$ for DIC ($\Delta\delta^{13}C_{DIC}$), values were mostly positive (n = 9), i.e., measured $\delta^{13}C_{DIC}$ was higher compared to estimated $\delta^{13}C_{DIC}$ due to conservative mixing. Deviation plot (ΔDIC vs. $\Delta\delta^{13}C_{DIC}$; Fig.3c) for samples of the Hooghly showed following patterns: (a) decrease in ΔDIC with increasing $\Delta\delta^{13}C_{DIC}$ (n = 5) indicating phytoplankton productivity and/or outgassing of CO_2 (PP/CO_2 OG) from water-atmosphere interface, (b) decrease in ΔDIC with decreasing $\Delta\delta^{13}C_{DIC}$ (n = 4) indicating carbonate precipitation (CP), and (c) increase of ΔDIC with increasing $\Delta\delta^{13}C_{DIC}$ (n = 4) representing carbonate dissolution (CD) within the system.

Based on these calculations, both organic and inorganic processes (productivity, carbonate precipitation and dissolution) along with physical processes (CO_2 outgassing across water-atmosphere interface) appeared to regulate DIC chemistry in the Hooghly estuary. Spatially, PP and CO_2 OG appeared to regulate DIC in the mixing zone (n = 5 out of 7) of the Hooghly. Earlier studies have advocated high phytoplankton productivity in non-limiting nutrient condition during postmonsoon in the Hooghly (Mukhopadhyay et al., 2002; Mukhopadhyay et al., 2006). However, based on the present data, particularly due to lack of direct PP measurements, it was difficult to spatially decouple PP and CO_2 outgassing in the mixing zone. In contrast to the mixing zone, CP and CD appeared to be dominant processes affecting estuarine DIC chemistry in the freshwater region of the Hooghly.

In mangrove-dominated estuaries of Sundarbans, our measured $\delta^{13}C_{DIC}$ values were within the range of that reported by Ray et al. (2018), whereas DIC concentrations were comparatively lower (DIC: 2130 ± 100 μmolkg^{-1}, $\delta^{13}C_{DIC}$: – 4.7 ± 0.7‰). Our data also showed similarity with Khura and Trang river, two mangrove-dominated rivers of peninsular Thailand flowing towards Andaman sea, although from hydrological prospective these two systems are contrasting in nature [Sundarbans: narrow salinity gradient (12.74 - 16.69) vs. Khura and Trang river: sharp salinity gradient (~ 0 – 35); Miyajima et al., 2009]. Like Hooghly, $\delta^{13}C_{DIC}$ - salinity relationship was statistically significant (r^2 = 0.55, p = 0.009) for the Sundarbans, but DIC - salinity relationship remained insignificant (p = 0.18) (Fig. 3d & 3e).

Given the dominance of mangrove in the Sundarbans, the role of mangrove derived OC mineralization may be important in regulating DIC chemistry in this ecosystem. Theoretically, $\Delta C_{Mangrove}$ for DIC ($\Delta DIC_{Mangrove}$) estimated based on DIC (ΔDIC_{M1}) and $\delta^{13}C_{DIC}$ (ΔDIC_{M2}) should be equal. The negative and unequal values of ΔDIC_{M2} (– 41 to 62 μM) and ΔDIC_{M1} (–

186 to 11 μM) indicate large DIC out-flux over influx through mangrove derived OC mineralization in this tropical mangrove system. The removal mechanisms of DIC include CO_2 outgassing across estuarine water-atmosphere boundary, phytoplankton uptake and export to adjacent continental shelf region (northern BOB, Ray et al., 2018). The evidence for CO_2 outgassing was found at almost all locations covered during the present study (10 out of 11 locations covered; see section 4.4). Also, a recent study by Ray et al. (2018) estimated DIC export (~ 3.69Tg C yr^{-1}) from the estuaries of Sundarbans as dominant form of C export. Although data for primary productivity is not available for the study period, earlier studies have reported postmonsoon as peak season for phytoplankton productivity (Biswas et al., 2007; Dutta et al., 2015). Given the evidences for presence of DIC removal processes in the Sundarbans, a comprehensive study focused on rate measurements of these processes with higher spatial and temporal coverage is desirable to understand the balance between influx and out-flux of DIC in the Sundarbans.

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 and DIC along with low pH and TAlk/DIC are general characteristics of groundwater, specially within carbonate aquifer region (Cai et al., 2003). Although all the parameters of groundwater 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 mean 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 may stand as a signal for influence of groundwater on estuarine DIC, with possibly higher influence at the Sundarbans than Hooghly as evident from the slope of the TAlk - DIC relationships (Hooghly: 0.98, Sundarbans: 0.03). In the Sundarbans, to the best of our knowledge, no report exists regarding groundwater discharge. Contradictory reports exist for the Hooghly, where Samanta et al. (2015) indicated groundwater contribution at low salinity regime (salinity < 10, same as our salinity range) based on 'Ca' measurement, which was not observed based on 'Ra' isotope measurement in an earlier study (Somayajulu et al., 2002). 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. A first-time baseline value for advective DIC influx from mangrove sediment to the estuary (F_{DIC}) via pore-water exchange was estimated during the present study using the following expression (Reay et al., 1995):

$$F_{DIC} = \text{Sediment porosity x Mean linear velocity x Mean pore water DIC conc.}$$

$$\text{Mean linear velocity} = \text{Pore water specific discharge / Sediment porosity}$$

Using pore-water specific discharge and porosity as 0.008 cm min^{-1} and 0.58 (Dutta et al., 2013, Dutta et al., 2015), respectively during postmonsoon and extrapolating the flux value over daily basis (i.e., for 12 hours as tides are semidiurnal in nature), mean F_{DIC} during postmonsoon was calculated as ~ 770.4 mmol m^{-2} d^{-1}. 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 ($p = 0.93$). A comprehensive investigation on ground and pore waters are needed to thoroughly understand their importance in controlling DIC chemistry of the Hooghly-Sundarbans system.

From the above discussion it appears that on an average ~ 327 µM higher DIC in the Hooghly compared to the Sundarbans may be due to cumulative interaction between freshwater content to the individual estuaries as well as degree of biogeochemical and hydrological processes. Relatively higher freshwater contribution in the Hooghly compared to the Sundarbans (as evident from salinity) as well as significant negative relationship between DIC - salinity proved significant impact of freshwater on DIC pool in the Hooghly. However, detailed quantification of other biogeochemical and hydrological processes is needed to decipher dominant processes affecting DIC dynamics in the Hooghly-Sundarbans system.

4.2 DOC in the Hooghly-Sundarbans

During the present study, DOC concentrations in the Hooghly estuary were higher compared previously reported by Ray et al. (2018) (226.9 ± 26.2 to 324 ± 27µM), whereas DOC in the Sundarbans were comparable with Ray et al. (2018) (262.5 ± 48.2µM). The marine and freshwater mixing did not appear to exert major control over DOC in the Hooghly-Sundarbans system as evident from lack of significant correlations between DOC and salinity (Hooghly freshwater: $r^2 = 0.33$, $p = 0.23$; Hooghly mixing region: $r^2 = 0.10$, $p = 0.50$; Sundarbans: $r^2 = 0.27$, $p = 0.10$, Fig.4a). Our observations showed similarity with other Indian estuaries (Bouillon et al., 2003) with opposite reports from elsewhere (Raymond and Bauer, 2001a, Abril et al., 2002). This indicates that DOC in this sub-tropical estuarine system is principally controlled by processes other than mixing of two water masses.

Although it is difficult to accurately decipher processes influencing DOC without $\delta^{13}C_{DOC}$ data, some insights may be obtained from estimated ΔC of DOC (ΔDOC). The estimated ΔDOC in the Hooghly indicated both net addition (n = 3) and removal (n = 3) of DOC in the freshwater zone (ΔDOC = – 0.16 to 0.11); whereas, only net addition was evident throughout the mixing zone (ΔDOC = 0.08 to 1.74). In the Sundarbans, except lower Thakuran (St. T3, ΔDOC_{M1} = – 20µM), net addition of mangrove derived DOC was estimated throughout (ΔDOC_{M1} = 2 - 134µM).

In an estuary, DOC can be added through *in situ* production (by benthic and pelagic primary producers), lysis of halophobic freshwater phytoplankton cells and POC dissolution. DOC can be removed through bacterial mineralization, flocculation as POC, and photo-oxidation (Bouillon et al., 2006). At the Hooghly - Sundarbans system, no evidence for freshwater phytoplankton ($\delta^{13}C$: – 33 to – 40‰; Freitas et al., 2001) was found from $\delta^{13}C_{POC}$, ruling out its potential effect on DOC. Although an indirect signal for phytoplankton productivity was observed in the freshwater region from $\delta^{13}C_{DIC}$ and POC relationship (r^2 = 0.68, p = 0.05), further evaluation of its impact on DOC was not possible due to lack of direct primary productivity measurements. Contradictory results exist regarding influence of phytoplankton productivity on DOC. Some studies did not find direct link between DOC and primary productivity (Boto and Wellington, 1988), whereas primary productivity mediated significant DOC formation (~ 8 - 40%) has been reported by others (Dittmar & Lara 2001a, Kristensen & Suraswadi 2002).

The DOC - pCO_2 relationship suggested inefficient bacterial DOC mineralization in the Hooghly (freshwater zone: p = 0.69, mixing zone: p = 0.67, Fig. 4b). However, significant positive relationship between these two in the Sundarbans (r^2 = 0.45, p = 0.02, Fig. 4c) indicated increase in aerobic bacterial activity with increasing DOC. In mangrove ecosystems, leaching of mangrove leaf litter as DOC is fast as ~ 30% of mangrove leaf litter leaching as DOC is reported within initial 9 days of degradation (Camilleri and Ribi, 1986). In the Sundarbans, mangrove litter fall peaks during postmonsoon (Ray et al. 2011) and its subsequent significant leaching as DOC was evident during the present study from comparatively higher DOC compared to POC (DOC:POC = 0.50 - 3.39, mean: 1.79 ± 0.94%). Our interpretation for Sundarbans corroborated with that reported by Ray et al. (2018) for the same system as well as Bouillon et al. (2003) for the Godavari estuary, South India.

Despite high water residence time in the Hooghly (~ 40 days during postmonsoon, Samanta et al., 2015) and in mangrove ecosystem like Sundarbans (Alongi et al., 2005, Singh et al., 2016), DOC photo-oxidation may not be so potent due to unstable estuarine condition in the Hooghly-Sundarbans system (Richardson number < 0.14) with intensive vertical mixing and longitudinal dispersion coefficients of 784 $m^2 s^{-1}$ (Goutam et al., 2015, Sadhuram et al., 2005). The unstable condition may not favor DOC - POC interconversion as well but mediated by charged complexes and repulsion - attraction interactions, the interconversion partly depends upon variation in salinity. More specifically, the interconversion is efficient during initial mixing of fresh (river) and seawater and the coagulation is mostly complete within salinity range 2 - 3. This appeared to be the case in the Hooghly, where DOC and POC was negatively correlated in the freshwater region ($r^2 = 0.86$, $p = 0.007$, Fig.4d), which was missing in the mixing region ($p = 0.43$) and in the Sundarbans ($p = 0.84$).

Although estimated ΔDOC indicated largely net DOC addition to the Hooghly-Sundarbans system, except leaf litter leaching in the Sundarbans, no significant evidence for other internal sources was found. This suggested potential contribution from external sources that may include industrial effluents and municipal wastewater discharge (i.e., surface runoff) in the freshwater region of the Hooghly (Table 1). However, there is no direct DOC influx data to corroborate the same. Relatively higher DOC compared to POC (DOC/POC > 1) at some locations (H2, H5, H6) may stand as a signal for higher DOC contribution at those locations, but it is not prudent to pinpoint its sources due to lack of isotopic data. Although anthropogenic inputs are mostly confined to freshwater region, relatively higher DOC in the mixing zone of the Hooghly compared to freshwater region suggested DOC input via some additional pathway, possibly groundwater discharge. The contribution of groundwater to the Hooghly estuary within the salinity range observed during the present study has been reported (Samanta et al., 2015). However, there is no report of groundwater mediated DOC influx to the estuary. For mangrove-dominated ecosystems like Sundarbans, a recent study by Maher et al. (2013) estimated ~ 89 - 92% of the total DOC export to be driven by groundwater advection. To understand spatial variability of DOC chemistry in the Hooghly-Sundarbans system, a thorough investigation related to groundwater and surface runoff mediated DOC flux is warranted.

Overall, on an average ~ 40% higher DOC in the Hooghly compared to the Sundarbans appeared to be due to cumulative effect of freshwater contributions, higher anthropogenic inputs, influence of biogeochemical processes and groundwater contribution. However, DOC inputs via other pathways may be dominant over freshwater mediated input as evident from insignificant DOC - salinity relationship during the present study. To quantitatively understand the relative control of the above-mentioned contributors to the DOC pool in the Hooghly-Sundarbans system, the individual components need to be studied in detail.

4.3 Major drivers of particulate organic matter

The average POC during the present study was considerably higher compared to that reported by Ray et al. (2018) for the Hooghly-Sundarbans (Hooghly: 40.3 ± 1.1 to 129.7 ± 6.7µM, Sundarbans: 45.4 ± 7.5µM). However, the present POC values were within the range reported for a large set of Indian estuaries (POC: 51 - 750 µM; Sarma et al., 2014). No significant SPM-salinity or POC-salinity relationship was observed during the present study (Fig. 5a & 5b), except for a moderate negative correlation between POC and salinity (r^2 = 0.62, p = 0.06) in the freshwater region of the Hooghly. This inverse relationship may be linked to freshwater mediated POC addition. Also, as described earlier, contribution of POC via surface-runoff is also a possibility in this region due to presence of several industries and large urban population (St: H2: Megacity Kolkata) that discharge industrial effluent and municipal wastewater to the estuary on regular basis (Table 1). Primary signal for surface runoff mediated POC addition was evident in the freshwater zone where ~ 61% and ~ 43% higher POC at 'H3' and 'H4' compared to an upstream location (St. H2) was observed. However, based on the present data, it is not possible to decouple freshwater and surface runoff mediated POC input to the Hooghly estuary. Relatively lower contribution of POC to the SPM pool of the Sundarbans (0.66 - 1.23%) compared to the Hooghly (0.96 - 4.22%; Fig. 5c) may be due to low primary production owing to high SPM load (Ittekkot and Laane, 1991) as observed in the mangrove-dominated Godavari estuary in the southern India (Bouillon et al., 2003).

In general, wide range for $\delta^{13}C$ (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 different researchers in different ecosystems (Smith and Epstein, 1971, Hedges et al., 1997, Zhang et al., 1997, Dehairs et al., 2000, Bouillon et al., 2002). In the Hooghly, our measured $\delta^{13}C_{POC}$ suggested influx of POC via freshwater runoff as well as terrestrial C_3 plants. Additionally, the estuary was also anthropogenically stressed during postmonsoon with measured $\delta^{13}C_{POC}$ within the range reported for sewage ($\delta^{13}C$ ~ –28 to –14 ‰, Andrews et al., 1998). In the mixing zone of the Hooghly, significantly lower $\delta^{13}C_{POC}$ at 'H11' and 'H12' compared to other sampling locations may be linked to localized ^{13}C depleted organic C influx to the estuary from adjacent mangrove and anthropogenic discharge, respectively.

In the estuaries of Sundarbans, isotopic signatures of POC showed similarity with terrestrial C_3 plants. Interestingly, despite being mangrove-dominated estuary (salinity: 12.74 - 16.55) no clear signature of either freshwater or mangrove ($\delta^{13}C$: mangrove leaf ~ –28.4‰, soil ~ –24.3‰, Ray et al., 2015, 2018) borne POC was evident from $\delta^{13}C_{POC}$ values, suggesting towards the possibility of significant POC modification within the system. Modification of POC within the estuaries of Indian sub-continent have been reported earlier (Sarma et al., 2014). Inter-estuary comparison revealed relatively lower average $\delta^{13}C_{POC}$ at the Hooghly (mean $\delta^{13}C_{POC}$: –24.87 ± 0.89‰) compared to the Sundarbans (mean $\delta^{13}C_{POC}$: −23.36 ± 0.32‰), which appeared to be due to differences in degree of freshwater contribution, anthropogenic inputs (high in Hooghly vs. little/no in Sundarbans), nature of terrestrial C_3 plant material (mangrove in the Sundarbans vs. others in Hooghly) as well as responsible processes for POC modification within the system.

To decipher processes involved in POC modification, estimated ΔC for POC (ΔPOC) in the Hooghly indicated both net addition (n = 3) and removal (n = 3) of POC in the freshwater region (ΔPOC = – 0.45 to 0.48), whereas removal (n = 6) dominated over addition (n = 1) in the mixing region (ΔPOC = – 0.39 to 0.07). In an estuary, POC may be added through freshwater and surface runoff mediated inputs, phytoplankton productivity, and DOC flocculation. The removal of POC is likely due to settling at subtidal sediment, export to adjacent continental shelf region, modification via conversion to DOC and mineralization in case of oxygenated estuary.

The plot between $\Delta\delta^{13}C$ for POC ($\Delta\delta^{13}C_{POC}$) and ΔPOC (Fig. 5d) indicated different processes to be active in different regions of the Hooghly estuary. Decrease in ΔPOC with increase in $\Delta\delta^{13}C_{POC}$ (RR; n = 4 for mixing region and n = 1 for freshwater region) suggested modification of POC due to aerobic respiration (or mineralization). This process did not appear to significantly impact estuarine CO_2 pool as evident from the POC - pCO_2 relationship (freshwater region: p = 0.29, mixing region: p = 0.50; Fig. 5e). Decrease in both ΔPOC and $\Delta\delta^{13}C_{POC}$ (SD; n = 2 for mixing region and n = 2 for freshwater region) supported settling of POC to sub-tidal sediment. Despite high water residence time (~ 40 days during postmonsoon, Samanta et al., 2015), this process may not be effective in the Hooghly due to unstable estuarine condition (described earlier). Increase in ΔPOC with decrease in $\Delta\delta^{13}C_{POC}$ (SR, FR & PP; n = 2 for freshwater region) indicated increase of POC via surface and freshwater runoff as well as phytoplankton productivity. Increase in both ΔPOC and $\Delta\delta^{13}C_{POC}$ (n = 1 for mixing region and n = 1 for freshwater region) may be linked to DOC to POC conversion by flocculation.

In the Sundarbans, negative and lower ΔPOC_{M2} (–209 to –28μM) compared to ΔPOC_{M1} (–35 to 327μM) suggested DIC like behavior, i.e., simultaneous removal or modification along with addition of mangrove derived POC. No evidence for *in situ* POC-DOC exchange was obvious based on POC-DOC relationship; however, signal for POC mineralization was evident in the Sundarbans from POC - pCO_2 relationship (r^2 = 0.37, p = 0.05, Fig.5f). Similar to the

Hooghly, despite high water residence time in mangroves (Alongi et al., 2005, Singh et al., 2016), unstable estuarine condition may not favor efficient settlement of POC at sub-tidal sediment. The export of POC from the Hooghly-Sundarbans system to the northern BOB, without significant *in situ* modification, is also a possibility. This export has been estimated to be ~0.02 - 0.07Tg and ~ 0.58Tg annually for the Hooghly and Sundarbans, respectively (Ray et al. 2018).

4.4 pCO_2 and FCO_2 in the Hooghly-Sundarbans

The estimated pCO_2 for the Hooghly-Sundarbans system were in the range reported for other tidal estuaries of India (Cochin estuary: 150-3800µatm, Gupta et al., 2009; Mandovi - Zuari estuary: 500-3500µatm, Sarma et al., 2001). In the Sundarbans, barring three locations (S3, T3 and M2), a significant negative correlation between pCO_2 and %DO ($r^2 = 0.76$, $p = 0.005$; Figure not given) suggested presence of processes, such as OM mineralization, responsible for controlling both CO_2 production and O_2 consumption in the surface estuarine water. Furthermore, significant positive correlation between ECO_2 and AOU ($ECO_2 = 0.057AOU + 1.22$, $r^2 = 0.76$, $p = 0.005$, $n = 8$; Fig.6a) confirmed the effect of aerobic OM mineralization on CO_2 distribution, particularly in the upper region of the Sundarbans. Our observations were in agreement with a previous study in the Sundarbans (Akhand et al., 2016) as well as another sub-tropical estuary, Pearl River estuary, China (Zhai et al., 2005). However, relatively lower slope for ECO_2 - AOU relationship (0.057) compared to the slope for Redfield respiration in HCO_3^- rich environment [$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 18HCO_3^{2-} \rightarrow 124CO_2 + 140H_2O + 16NO_3^- + HPO_4^{2-}$; $\Delta CO_2: (-\Delta O_2) = 124/138 = 0.90$, Zhai et al., 2005] suggested lower production of CO_2 than expected from Redfield respiration. This may be linked to formation of low molecular weight OM instead of the final product (CO_2) during aerobic OM respiration (Zhai et al., 2005). Moreover, pCO_2 - salinity relationship ($p = 0.18$, Fig.6b) confirmed no significant effect of fresh and marine water contribution on variability of pCO_2 in the Sundarbans. Other potential source of CO_2 to mangrove-dominated Sundarbans could be groundwater (or pore water) exchange across intertidal mangrove sediment-water interface. Although based on our own dataset, it is not possible to confirm the same. However, relatively higher pCO_2 levels during low-tide compared to high-tide at Matla estuary in the Sundarbans (Akhand et al. 2016) as well as in other mangrove systems worldwide (Rosentreter et al., 2018, Call et al., 2015, Bouillon et al., 2007) suggested groundwater (or pore water) exchange to be a potential CO_2 source in such systems.

Unlike Sundarbans, ECO_2 - AOU relationship did not confirm significant impact of OM respiration on CO_2 in either freshwater ($p = 0.50$) or mixing regions ($p = 0.75$) of the Hooghly (Fig. 6c). Overall, pCO_2 in the freshwater region of the Hooghly was significantly higher compared to the mixing zone (Table 3), which may be linked to CO_2 supply in the freshwater region through freshwater or surface runoff from adjoining areas (Table - 1). Inter-estuary comparison of pCO_2 also revealed ~1291 µatm higher pCO_2 in the Hooghly compared to the Sundarbans, which was largely due to significantly higher pCO_2 in freshwater region of the Hooghly (Table 2 & 3). Lack of negative correlation between pCO_2 - salinity in freshwater region (Fig. 6d) of the Hooghly suggested limited contribution of CO_2 due to freshwater inputs. Therefore, CO_2 supply via surface runoff may be primary reason for higher pCO_2 in the Hooghly estuary.

Positive mean FCO_2 clearly suggested the Hooghly-Sundarbans system to be a net source of CO_2 to the regional atmosphere during postmonsoon (Fig.6e & 6f). Specifically, from regional climate and environmental change perspective, anthropogenically influenced Hooghly estuary was a relatively greater source of CO_2 to the regional atmosphere compared to the mangrove-dominated Sundarbans as evident from significantly higher CO_2 emission flux from the Hooghly ($[FCO_2]_{Hooghly}$: $[FCO_2]_{Sundarbans}$ = 17). However, despite being a CO_2 source, FCO_2 measured for the estuaries of Sundarbans were considerably lower compared to global mean FCO_2 reported for mangrove-dominated estuaries (~ 43-59 mmol C m^{-2} d^{-1}; Call et al., 2015). Similarly, FCO_2 measured for the Hooghly estuary were 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 difference in FCO_2 between Hooghly and Sundarbans may be due to variability in pCO_2 level as well as micrometeorological and physicochemical parameters controlling gas transfer velocity across water-atmosphere interface. Quantitatively, the difference in 'k' values for the Hoogly and Sundarbans were not large ($k_{Sundarbans} - k_{Hooghly}$ ~ 0.031 $cmhr^{-1}$). Therefore, large difference in FCO_2 between these two estuarine systems may be due to difference in pCO_2. Taken together, supporting our hypothesis, it appears that differences in land use and degrees of anthropogenic influence have the potential to alter the C biogeochemistry of aquatic ecosystems with anthropogenically stressed aquatic systems acting as a relatively greater source of CO_2 to the regional atmosphere than mangrove-dominated ones.

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.
- Coupled with freshwater contribution, inorganic and organic C metabolism appeared to be dominant processes affecting DIC in the Hooghly. However, in the Sundarbans, significant DIC removal over addition was noticed. Influence of groundwater on estuarine DIC biogeochemistry was also observed with relatively higher influence at the Sundarbans.
- Higher DOC level in the Hooghly appeared to be regulated by coupled interactions among anthropogenic inputs, biogeochemical processes and groundwater contribution rather than freshwater mediated inputs.
- Signatures of freshwater runoff, terrestrial C_3 plants, and anthropogenic discharge were found in POC of the Hooghly, whereas evidence for only C_3 plants were noticed at the Sundarbans with possible POC modification.
- Organic matter mineralization and surface run-off from adjoining areas appeared to be dominant controlling factor for $p\text{CO}_2$ in the Sundarbans and Hooghly, respectively, with higher average $p\text{CO}_2$ in the Hooghly compared to 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, suggesting dominance of anthropogenically stressed estuarine system over mangrove-dominated one from regional climate change perspective.

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Data availability

Data used in the manuscript is presented in tables (Table 2, Table 3, and Table 4) 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: %DO - salinity at the Hooghly-Sundarbans systems (Green, grey and blue colors indicate freshwater region of the Hooghly, mixing region of the Hooghly and Sundarbans, respectively).

Fig. 3: (a) DIC - salinity in the Hooghly (solid line indicates estimated concentrations due to conservative mixing), (b) $\delta^{13}C_{DIC}$ - salinity in the Hooghly estuary (solid line indicates estimated $\delta^{13}C_{DIC}$ due to conservative mixing), (c) ΔDIC - Δ $\delta^{13}C_{DIC}$ in the Hooghly estuary (PP = Phytoplankton productivity, OG = outgassing, CD = carbonate dissolution, CP = carbonate precipitation, OM Res. = Respiration of organic matter), (d) DIC - salinity in the Sundarbans, and (e) $\delta^{13}C_{DIC}$ - salinity in the Sundarbans (Green, grey and blue color indicates freshwater region of the Hooghly, mixing region of the Hooghly and the Sundarbans, respectively).

Fig.4: (a) DOC - salinity in the Hooghly-Sundarbans, (b) DOC - pCO_2 in the Hooghly, (c) DOC - pCO_2 in the Sundarbans, and (d) DOC - POC in the Hooghly-Sundarbans (Green, grey and blue color indicates freshwater region of the Hooghly, mixing region of the Hooghly and the Sundarbans, respectively).

Fig.5: (a) SPM - salinity, (b) POC - salinity, (c) %POC/SPM – salinity, (d) ΔPOC - Δ $\delta^{13}C_{POC}$ in Hooghly (RR - aerobic respiration, SD - deposition at sub-tidal sediment, SR - surface runoff, FR - freshwater runoff and PP - phytoplankton productivity), (e) POC - pCO_2 in Hooghly and (f) POC - pCO_2 in Sundarbans (Green, grey and blue color indicates freshwater region of the Hooghly, mixing region of the Hooghly and the Sundarbans, respectively).

Fig. 6: (a) ECO_2 - AOU in the Sundarbans (b) pCO_2 - salinity in the Sundarbans (c) ECO_2 - AOU in the Hooghly (d) pCO_2 - salinity in the Hooghly (e) FCO_2 - salinity in the Hooghly, and (f) FCO_2 - salinity in the Sundarbans (Green, grey and blue color indicate freshwater region of the Hooghly, mixing region of the Hooghly and the Sundarbans, respectively).

Table - 1: General characteristic of the Hooghly estuary and the estuaries of Sundarbans.

Parameters	**Hooghly**	**Sundarbans**
Nutrients (postmonsoon)	DIN: 14.72 ± 1.77 to 27.20 ± 2.05μM DIP: 1.64 ± 0.23 to 2.11 ± 0.46μM DSi: 77.75 ± 6.57 to 117.38 ± 11.54μM (Mukhopadhyay et al., 2006)	DIN: 11.70 ± 7.65μM DIP: 1.01 ± 0.52μM DSi: 75.9 ± 36.9μM (Biswas et al., 2004)
Chl*a* (postmonsoon)	Chl-a: 2.35 – 2.79 mgm^{-3} (Mukhopadhyay et al., 2006)	Chl*a*: 7.88 ± 1.90 mgm^{-3} (Dutta et al., 2015)
Population density	North 24 Parganas and Hooghly: 2500 km^{-2}, Kolkata: 22000 km^{-2}, Howrah: 3300km^{-2}, South 24 Parganas: 820 km^{-2}	No major Cities and town
Freshwater discharge (postmonsoon)	3070 - 7301 million m^3 (Rudra et al., 2014)	No information available
Catchment area	6 x $10^4 km^2$ (Sarkar et al., 2017)	No information available
Industrial and municipal wastewater discharge	1153.8Million L d^{-1} (Ghosh, 1973; Khan, 1995)	No information available
Dissolved metal flux	Increased from 230 – 1770% annually (Samanta and Dalai, 2018)	No information available

Table - 2: Physicochemical parameters, inorganic and organic C related parameters, and CO_2 exchange fluxes across water-atmosphere at the estuaries of Sundarbans. Here, water temperature (W_T), DO, isotopic compositions, DIC, DOC, POC, pCO_2 and FCO_2 are presented in '°C' 'mgL^{-1}', '‰', 'µM', 'µM', '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**
S1	28.50	12.74	6.65	8.02	1780	– 5.59	278	154	– 22.85	536	26.5
S2	28.00	16.02	6.65	8.02	1703	– 4.33	267	124	– 23.54	561	30.3
S3	28.00	16.69	6.61	8.12	1700	– 4.29	197	114	– 23.43	395	0.9
S4	29.00	15.25	6.46	8.01	1861	– 5.27	315	93	– 23.68	543	27.6
T1	29.00	14.30	6.56	8.05	1757	– 5.57	259	80	– 23.62	490	18.1
T2	29.00	15.51	6.74	8.07	1727	– 4.79	182	106	– 23.21	456	11.9
T3	28.50	16.55	6.46	8.11	1683	– 4.39	154	154	– 22.97	403	2.4
M1	28.00	15.14	6.99	8.07	1711	– 5.93	282	264	– 23.07	443	9.4
M2	28.00	15.14	6.91	8.12	1735	– 4.63	219	436	– 23.15	376	-2.6
M3	28.00	15.23	7.46	8.13	1736	– 5.30	222	287	– 23.62	401	1.9
M4	28.50	14.78	6.84	8.04	1920	– 5.38	215	96	– 23.82	503	20.3

Table - 3: Physicochemical parameters, inorganic and organic C related parameters, and CO_2 exchange fluxes across water-atmosphere at the Hooghly estuary. Here, water temperature (W_T), DO, all isotopic compositions, DIC, DOC, POC, pCO_2 and FCO_2 are presented in '°C' 'mgL^{-1}', '‰', 'µM', 'µM', '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	2700	– 6.98	244	313	– 25.34	2036	285.2
H2	33.0	0.07	6.11	7.71	1678	– 8.38	304	177	– 25.19	2316	343.8
H3	31.0	0.08	6.45	7.83	2498	– 6.70	235	286	– 25.95	2490	355.4
H4	31.0	0.13	5.24	7.73	2446	– 7.38	243	254	– 25.40	2691	389.2
H5	31.0	0.19	5.38	7.77	2355	– 7.56	340	130	– 25.67	2123	293.1
H6	30.5	0.32	5.66	7.31	2157	– 8.61	308	116	– 24.07	4678	717.5
H7	31.5	5.83	6.71	7.68	1829	– 6.79	662	145	– 24.70	1184	132.0
H8	31.0	5.19	7.14	7.31	2023	– 6.78	354	139	– 23.47	3153	455.8
H9	31.5	9.08	6.62	7.90	1915	– 6.08	332	161	– 23.53	665	44.9
H10	31.5	9.72	6.17	8.08	1787	– 5.78	249	95	– 24.06	452	10.1
H11	31.0	8.43	6.37	8.07	1977	– 7.21	358	95	– 25.94	486	15.6
H12	31.5	5.83	7.40	8.29	1871	– 6.60	260	133	– 26.28	274	-19.3
H13	31.0	10.37	7.00	8.24	1843	– 5.57	394	129	– 24.72	267	-19.8

Table - 4: The DIC concentrations and $\delta^{13}C_{DIC}$ of groundwater (GW) and pore-water (PW) samples collected around Hooghly-Sundarbans system.

Ecosystem	Station	DIC (µM)	$\delta^{13}C_{DIC}$ (‰)
Hooghly	H3GW	11756	– 12.66
	H4GW	6230	– 7.85
	H5GW	6327	– 8.96
	H6GW	7026	– 11.27
	H7GW	5655	– 6.91
	H11GW	9115	– 7.67
	H12GW	6858	– 7.49
	H13GW	7258	– 7.21
	Gangasagar GW	7246	– 6.67
Sundarbans	Lothian GW	7524	– 6.84
	Lothian PW	13425	– 18.05
	Kalash GW	13599	– 6.69
	Virat Bazar GW	8300	– 10.56

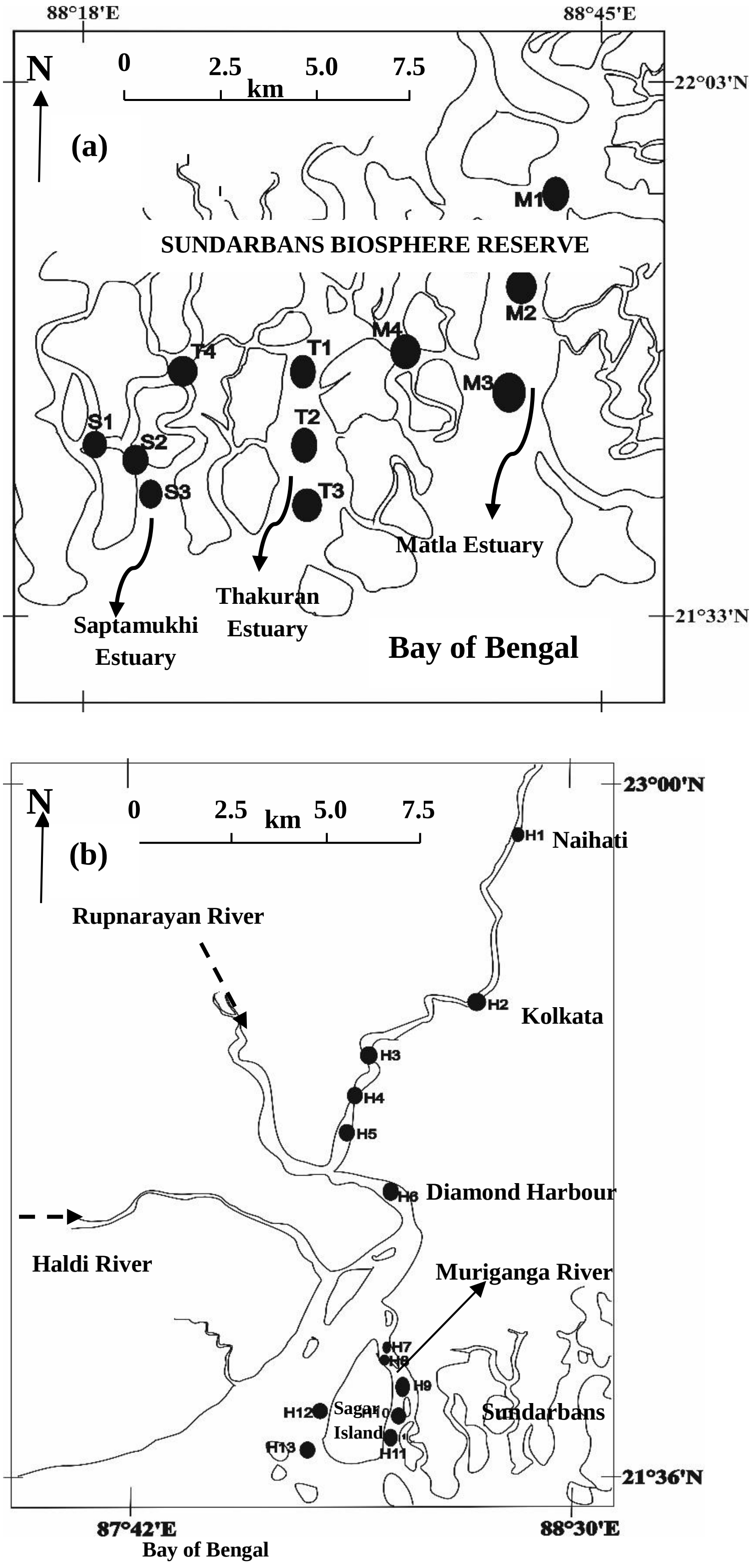
88°18'E
88°45'E
22°03'N
21°33'N
N
0
2.5
5.0
7.5
km
(a)
M1
SUNDARBANS BIOSPHERE RESERVE
M2
M4
T1
T4
M3
S1
T2
S2
S3
T3
Matla Estuary
Thakuran Estuary
Saptamukhi Estuary
Bay of Bengal
23°00'N
N
(b)
Naihati
Rupnarayan River
Kolkata
H1
H2
H3
H4
H5
Diamond Harbour
Haldi River
Muriganga River
H7
H9
H12
Sagar Island
Sundarbans
H11
H13
21°36'N
87°42'E
88°30'E
Bay of Bengal

Fig. 1

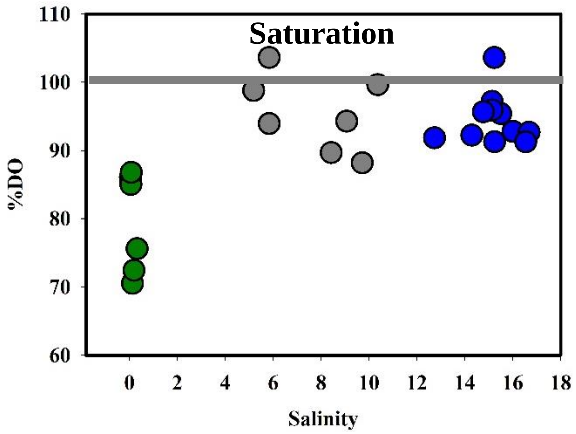

Fig. 2

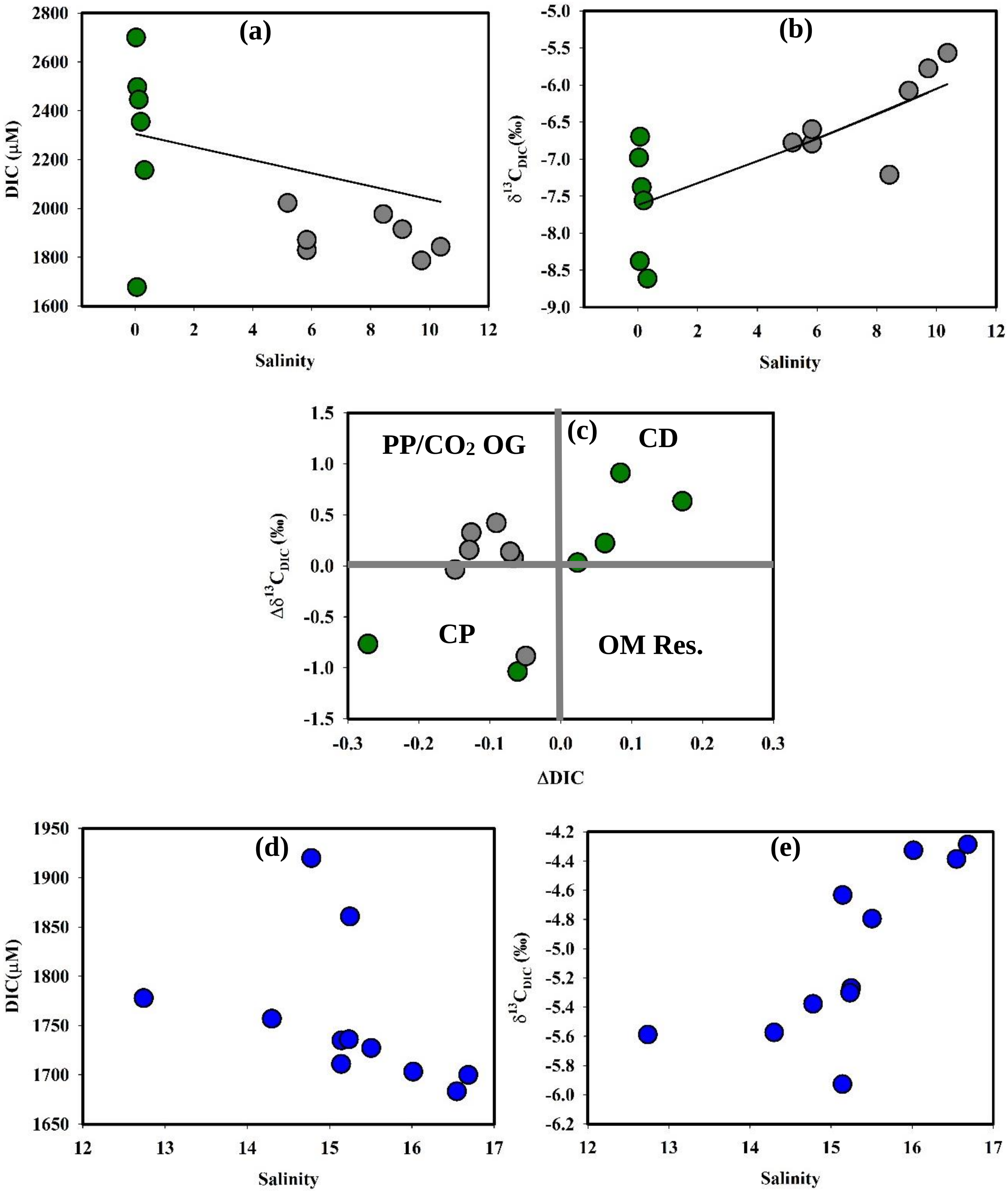
(a)
DIC (μM)
Salinity
(b)
δ13CDIC(‰)
Salinity
(c)
PP/CO2 OG
CD
CP
OM Res.
Δδ13CDIC (‰)
ΔDIC
(d)
DIC(μM)
Salinity
(e)
δ13CDIC (‰)
Salinity

Fig. 3

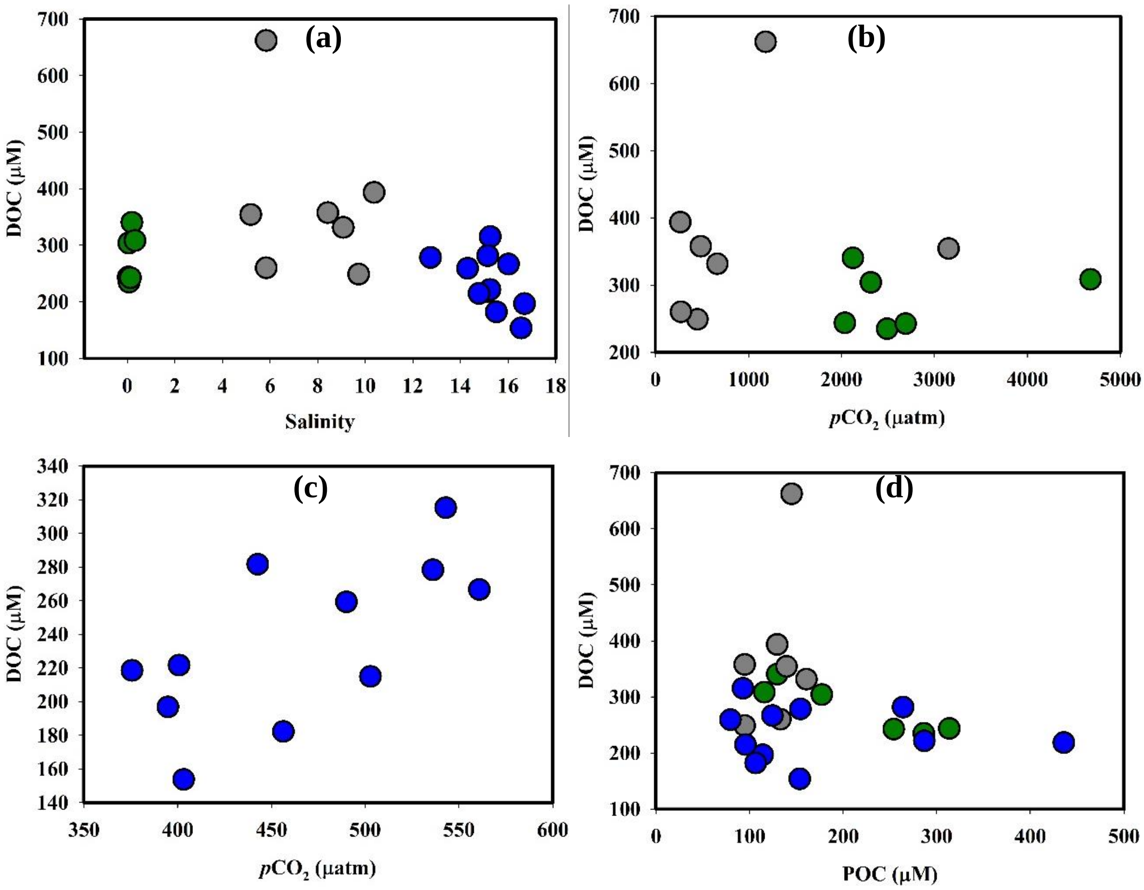
(a)
DOC (μM)
Salinity
(b)
DOC (μM)
pCO2 (μatm)
(c)
DOC (μM)
pCO2 (μatm)
(d)
DOC (μM)
POC (μM)

Fig. 4

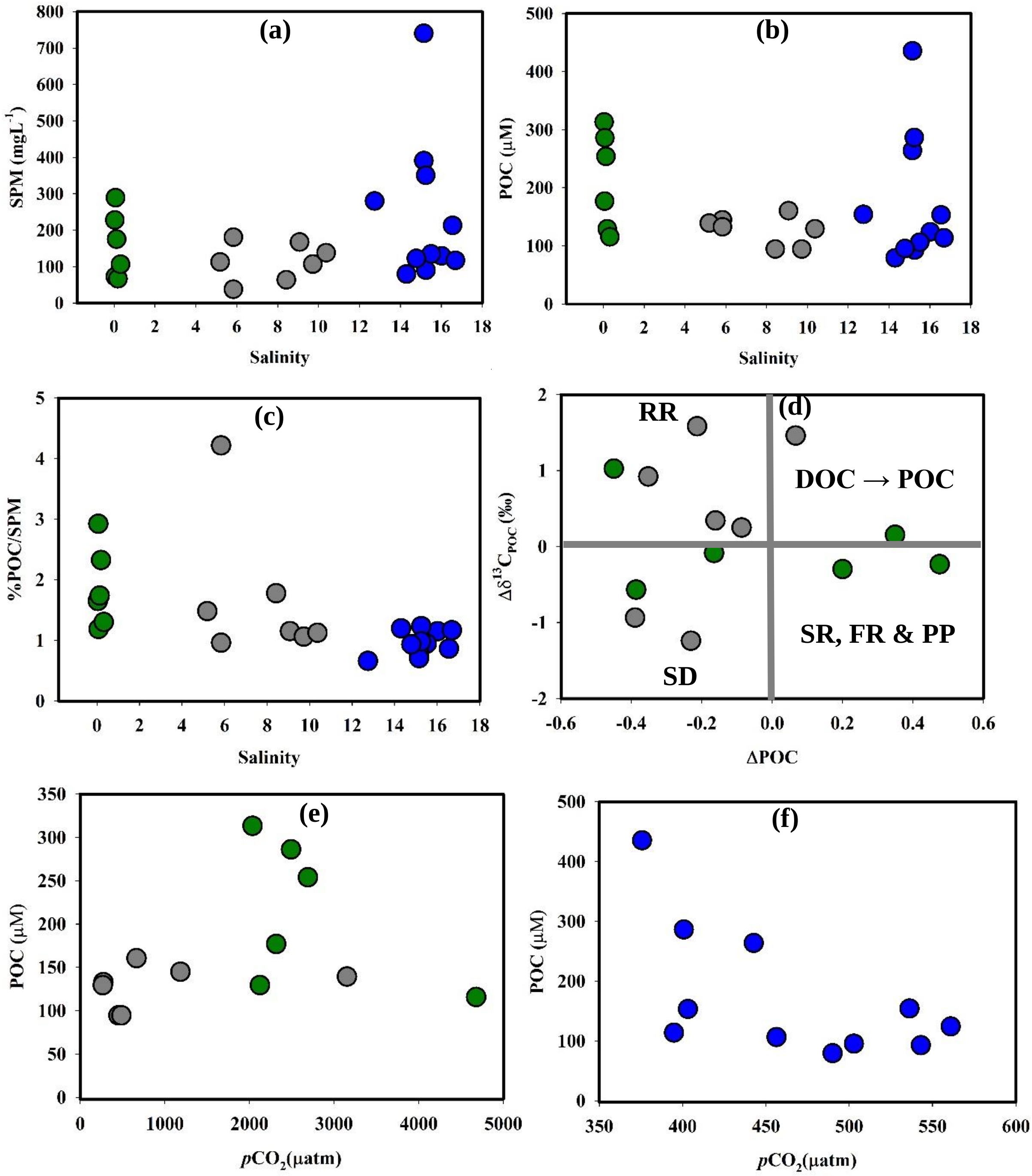
(a)
SPM (mgL-1)
Salinity
(b)
POC (μM)
Salinity
(c)
%POC/SPM
Salinity
(d)
RR
DOC → POC
SD
SR, FR & PP
Δδ13CPOC (‰)
ΔPOC
(e)
POC (μM)
pCO2(μatm)
(f)
POC (μM)
pCO2(μatm)

Fig. 5

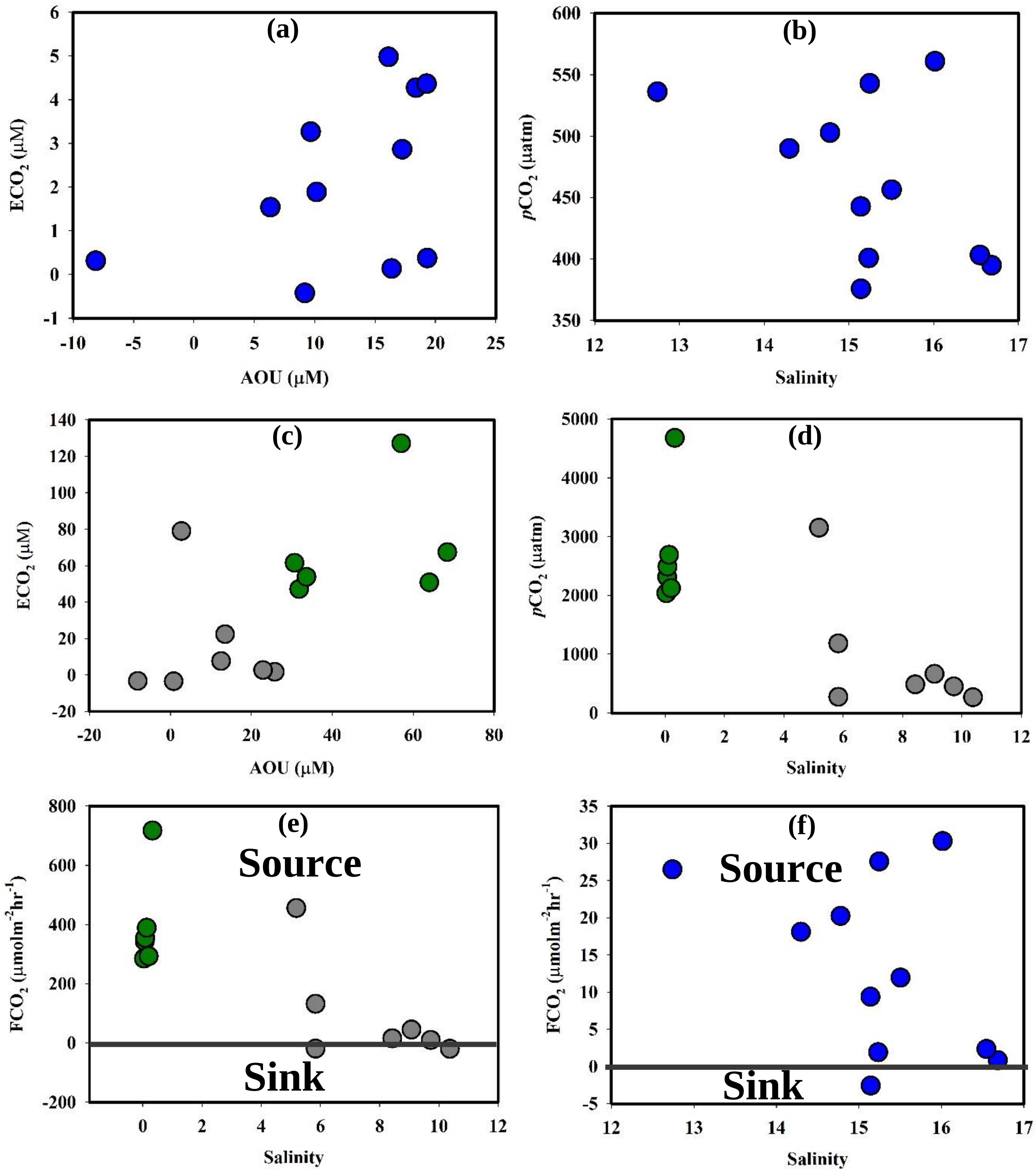
(a)
ECO2 (µM)
AOU (µM)
(b)
pCO2 (µatm)
Salinity
(c)
ECO2 (µM)
AOU (µM)
(d)
pCO2 (µatm)
Salinity
(e)
Source
Sink
FCO2 (µmolm-2hr-1)
Salinity
(f)
Source
Sink
FCO2 (µmolm-2hr-1)
Salinity

Fig. 6