The postmonsoon carbon biogeochemistry of the Hooghly-Sundarbans estuarine system 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 stresses by investigating anthropogenically influenced Hooghly estuary and mangrove-dominated estuaries of the Sundarbans in the north-eastern India. The salinity of well oxygenated estuaries of the Sundarbans (DO: 91 - 104%) varied over a narrow range (12.74 - 16.69) relative to the Hooghly (0.04 - 10.37). A mixing model suggested a combination of processes including freshwater intrusion, carbonate precipitation, and carbonate dissolution to be major factor controlling DIC dynamics in the freshwater regime of the Hooghly, whereas phytoplankton productivity and CO_2 outgassing dominated in the mixing regime. In the Sundarbans, removal of DIC (via CO_2 outgassing, phytoplankton uptake, and export to adjoining continental shelf region) dominated over its addition through mineralization of mangrove derived organic C. The concentration of DOC in the Hooghly was ~ 40% higher than in the Sundarbans, which was largely due to cumulative effect of anthropogenic inputs, DOC-POC interconversion, and groundwater contribution rather than freshwater mediated input. The measured $\delta^{13}C_{POC}$ in the Hooghly suggested particulate organic matter contributions from different sources (freshwater runoff, terrestrial C_3 plants, and anthropogenic discharge), whereas the contribution from C_3 plants was dominant 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 modification due to degradation by respiration. The average pCO_2 in the Hooghly was higher by ~ 1291 µatm compared to the Sundarbans with surface runoff and organic matter degradation by respiration as dominant factors controlling pCO_2 in the Hooghly and Sundarbans, respectively. The entire Hooghly-Sundarbans system acted as a source of CO_2 to the regional atmosphere with ~ 17 times higher emission from the Hooghly compared to the Sundarbans. Taken together, the cycling of C in estuaries having different levels of anthropogenic influences is evidently different with significantly higher CO_2 emission from the anthropogenically influenced estuary than the mangrove-dominated ones.

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 ~ 0.53 Pg C to the estuaries annually (Huang et al., 2012). The majority of this exported C is in dissolved form [dissolved inorganic C (DIC): 0.21 Pg C yr^{-1} and dissolved organic C (DOC): 0.14 Pg C yr^{-1}] with some contribution as particulate [particulate organic C (POC): 0.13 Pg C yr^{-1} and particulate inorganic C (PIC): 0.05 Pg C yr^{-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 ± 72 Tg 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 forest 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 showed a significant imbalance 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 exports 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 mangroves to be responsible for 93 - 99% and 89 - 92% of total DIC and DOC exports to the coastal ocean, respectively (Maher et al., 2013). Upon extrapolating these C exports 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 either in complex 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, carbonate precipitation / dissolution and water-atmosphere CO_2 exchange occurring in the estuary 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 the Guanabara Bay, Brazil, which acts as a strong CO_2 sink enhanced by eutrophication (Cotovicz Jr. et al., 2015). Lack of ample rate measurements 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 coastal C 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). The estuaries located in the northern part of India have received limited attention, including adjacently located Hooghly estuary and the estuaries of Sundarbans, which are part of the Ganga-Brahmaputra river system (Fig. 1). Characteristically, the Hooghly and the estuaries of Sundarbans are different from each other. The Hooghly estuary experiences significantly higher anthropogenic influence compared to the mangrove-dominated Sundarbans as evidenced by high nutrient and freshwater inputs (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 are principally *jute* (*Corchorus olitorius*) based, which produce fabrics for packaging a wide range of agricultural and industrial commodities.

Earlier, the major focus of biogeochemical studies in the Hooghly and the estuaries of Sundarbans had been on biogeochemistry of 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 (Samanta et al., 2015; Ray et al., 2015, 2018; Akhand et al., 2016). Samanta et al. (2015) 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 the Hooghly-Sundarbans system have been reported by Ray et al. (2015, 2018). Barring Samanta et al. (2015), which has wider spatial and temporal coverages with respect to DIC in the Hooghly, other studies are severely limited in spatial coverage with focus on mid to lower parts 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.

The primary objective of the present study was to understand differences in varied aspects of C cycle (DIC, DOC, POC, and CO_2) of the Hooghly and the estuaries of 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 systems, we hypothesized C metabolism in these two estuaries to be very different with higher CO_2 exchange flux from anthropogenically influenced estuary compared to the mangrove-dominated one. Specifically, the major aims of the present study were to investigate: (a) factors controlling DIC and DOC dynamics in the region, (b) sources and fate of POC 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 the mangrove dominated estuaries of Indian Sundarbans and anthropogenically dominated Hooghly estuary in the northeastern India. The Sundarbans (21^{o}32' and 22^{o}40'N: 88^{o}05' and 89^{o}E, Fig. 1a), 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 the 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 the 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 leaf 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: ~150 km).

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: 5 L). 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 ^oC) 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: ± 0.1 mg L^{-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 µmol kg^{-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 (Fig. 1). Pore-water was also collected from lower littoral zone of the Lothian Island (one of the virgin island of the Indian Sundarbans, Fig. 1a) by digging a hole (~ 30 cm below the water table). It was not possible to collect pore-water samples from the mid and upper littoral zones of the island 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 ^{o}C for 6 hours) Whatman GF/F filters (pore size: 0.7 μm). Filtrates were kept for DOC analysis in brown bottles followed by immediate preservation via addition of H_3PO_4 (50 μL/15 mL sample) (Bouillon et al., 2003), whereas the residues were kept for particulate matter analysis. Collected DIC, DOC and SPM samples were properly preserved at 4 ^{o}C during transportation to the laboratory. Additionally, micrometeorological parameters associated with water-atmosphere CO_2 exchange flux computation 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 concentrations 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 Scientific MAT 253) 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 ^{o}C and final weights were noted. The SPM were calculated based on differences between final and initial weights of the filter paper and volumes of water filtered. For measurements of POC and $\delta^{13}C_{POC}$, filter papers containing SPM were de-carbonated (by HCl fumes) and analyzed using Elemental Analyzer (Flash 2000) attached to the continuous flow mass spectrometer (Thermo Scientific MAT 253) 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 were 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:

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

Where, K_H^{CO2} = CO_2 solubility. ‘k’ is the 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).

The % saturation of DO and apparent oxygen utilization (AOU, departure of dissolved O_2 from atmospheric equilibrium) were calculated as follows:

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

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

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 additions/removals 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, means of salinities, C concentrations, 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 the Hooghly, direct application of above-mentioned conservative mixing model was not justified for the 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 the estuaries of Sundarbans are offshoot of lower Hooghly estuary.

2.2.5 Computation of advective DIC input from mangrove forest to estuary

A first-time baseline value for advective DIC input from mangrove forest sediment to the adjoining estuary (F_{DIC}) via pore-water exchange was calculated following Reay et al. (1995):

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

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

3 Results

3.1 Environmental parameters

During the present study, water temperature did not show any distinct spatial trend and varied from 28 to 29 ^oC and 30.5 to 33 ^oC for the Sundarbans (Table 2) and Hooghly (Table 3), respectively. Salinity of the estuaries of Sundarbans varied over a narrow range (12.74 to 16.69; Table 2) with minimum at the upper estuarine locations throughout. A relatively sharp salinity gradient was noticed at the Hooghly estuary (0.04 to 10.37; Table 3). Based on the observed salinity gradient, the Hooghly estuary can be divided into two major salinity regimes: (a) freshwater regime (H1 - H6) and (b) mixing regime (H7 - H13; Fig. 1b). However, due to narrow salinity range, no such classification was possible for the estuaries of Sundarbans. Estuaries of Sundarbans were relatively well-oxygenated (DO = 91 to 104%) compared to the Hooghly (DO = 71 to 104%; Fig. 2). Both pH and TAlk in the Hooghly estuary (pH: 7.31 to 8.29, TAlk: 1797 to 2862 µeq L^{-1}, Table 3) showed relatively wider variation compared to the estuaries of Sundarbans (pH: 8.01 to 8.13, TAlk: 2009 to 2289 µeq L^{-1}; Table 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 = 1683 to 1920 µM, mean: 1756 ± 73 µM; $\delta^{13}C_{DIC}$ = – 5.93 to – 4.29‰, mean: – 5.04 ± 0.58‰, Table 2) 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 3). In the Hooghly, DIC was relatively higher in the freshwater regime compared to the mixing regime, whereas reverse was observed for $\delta^{13}C_{DIC}$. 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 lower $\delta^{13}C_{DIC}$ 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 to 662 µM; Table 3) reaching peak in the mixing regime.

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 mg L^{-1}, mean: 241 ± 197 mg L^{-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 to 289 mg L^{-1} and 95 to 313 µM (Table 3), respectively; reaching maximum at the freshwater regime. 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 – 23.47‰ (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 561 µatm (mean: 464 ± 66 µatm; Table 2) with no spatial pattern. Compared to the Sundarbans, ~ 3.8 times higher pCO_2 was estimated in the Hooghly estuary (267 to 4678 µatm; Table 3) reaching its peak in the freshwater regime. Except one location at the Sundarbans (M2: – 42 µM) and two locations in the mixing regime 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 µmol m^{-2} hr^{-1}; mean: 231 µmol m^{-2} hr^{-1}; Table 3) was ~ 17 times higher than the mangrove dominated estuaries of the Indian Sundarbans (FCO_2: – 2.6 to 30.3 µmol m^{-2} hr^{-1}; Table 2). Spatially, in the Hooghly, higher FCO_2 was noticed in the freshwater regime (285.2 to 717.5 µmol m^{-2} hr^{-1}) compared to the mixing regime, while no such distinct spatial trend was observed at the Sundarbans.

4 Discussion

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

4.1 Major drivers of DIC dynamics

DIC concentrations observed in this study for the Hooghly were higher than that reported by Samanta et al. (2015) for the same season (DIC: 1700 to 2250 µM), whereas observed $\delta^{13}C_{DIC}$ were within their reported range ($\delta^{13}C_{DIC}$: – 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), rationalizing the application of two end member mixing model. Application of two end member mixing model to decipher processes influencing DIC chemistry has been done earlier in the Hooghly estuary (Samanta et al., 2015).

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 regime of the Hooghly, whereas only removal was evident in the mixing regime. 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 across water-atmosphere interface, (b) decrease in ΔDIC with decreasing $\Delta\delta^{13}C_{DIC}$ (n = 4) indicating carbonate precipitation, and (c) increase of ΔDIC with increasing $\Delta\delta^{13}C_{DIC}$ (n = 4) representing carbonate dissolution 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, phytoplankton productivity and/or outgassing of CO_2 appeared to regulate DIC in the mixing regime (n = 5 out of 7) of the Hooghly. Earlier studies have advocated for 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 primary productivity measurements, it was difficult to spatially decouple individual contributions of primary productivity and CO_2 outgassing in the mixing regime. In contrast to the mixing regime, carbonate precipitation and dissolution appeared to be dominant processes affecting DIC chemistry in the freshwater regime of the Hooghly.

In mangrove-dominated estuaries of the Sundarbans, observed $\delta^{13}C_{DIC}$ during this study were within the range ($\delta^{13}C_{DIC}$: – 4.7 ± 0.7‰) reported by Ray et al. (2018), whereas observed DIC concentrations were lower than their estimates (DIC: 2130 ± 100 µmol kg^{-1}). 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 to 16.69) vs. Khura and Trang river: sharp salinity gradient (~ 0 to 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 mangroves in the Sundarbans, the role of mangrove derived organic carbon (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 mineralization of mangrove derived OC in this tropical mangrove system. The removal mechanisms of DIC include CO_2 outgassing across estuarine water-atmosphere boundary, phytoplankton uptake and export to the 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 (~ 3.69 Tg C yr^{-1}) from the estuaries of Sundarbans as the 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 that measures rates of these processes with higher spatial and temporal coverages 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 a 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 (i.e., tidal pumping). 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 on 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 that measures rates of ground and pore waters mediated DIC additions is needed to thoroughly understand their importance in controlling DIC chemistry of the Hooghly-Sundarbans system.

From the above discussion, it appears that higher DIC in the Hooghly compared to the Sundarbans may be due to cumulative interactions 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, quantifications of other biogeochemical and hydrological processes are needed to decipher dominant processes affecting DIC dynamics in the Hooghly-Sundarbans system.

4.2 DOC in the Hooghly-Sundarbans

In the Hooghly, DOC concentrations observed during this study were higher than the range (226.9 ± 26.2 to 324 ± 27 µM) reported by Ray et al. (2018), whereas observed DOC in the Sundarbans were comparable with their estimates (262.5 ± 48.2 µM). The marine and fresh water 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 regime: $r^2 = 0.33$, $p = 0.23$; Hooghly mixing regime: $r^2 = 0.10$, $p = 0.50$; Sundarbans: $r^2 = 0.27$, $p = 0.10$, Fig. 4a). Our observation showed similarity with other Indian estuaries (Bouillon et al., 2003) with opposite reports from elsewhere (Raymond and Bauer, 2001, 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 regime (ΔDOC = – 0.16 to 0.11); whereas, only net addition was evident throughout the mixing regime (ΔDOC = 0.08 to 1.74). In the Sundarbans, except lower Thakuran (St. T3, $\Delta\ DOC_{M1}$ = – 20 µM), net addition of mangrove derived DOC was estimated throughout (ΔDOC_{M1} = 2 to 134 µM).

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 regime 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 measurement. 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 significant contribution of phytoplankton production to build DOC pool (~ 8 to 40%) has been reported by others (Dittmar and Lara, 2001; Kristensen and Suraswadi, 2002).

In a nutrient rich estuary like Hooghly, lack of significant relationship between DOC - pCO_2 (freshwater regime: p = 0.69, mixing regime: p = 0.67, Fig. 4b) suggested either inefficient bacterial DOC mineralization or significant DOC mineralization compensated by phytoplankton CO_2 uptake. 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 leaf litter fall peaks during postmonsoon (Ray et al. 2011) and its subsequent significant leaching as DOC was evident during the present study from relatively higher DOC compared to POC (DOC:POC = 0.50 to 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 the 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) having intensive vertical mixing with 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 mostly completes within salinity range 2 - 3. This appeared to be the case in the Hooghly, where DOC and POC were negatively correlated in the freshwater regime ($r^2 = 0.86$, $p = 0.007$, Fig. 4d) but not in the mixing regime ($p = 0.43$) or 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 regime of the Hooghly (Table 1). However, there is no direct DOC influx data available to corroborate the same. Relatively higher DOC compared to POC (DOC/POC > 1) at some locations (H2, H5, H6) of the freshwater regime 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. Considering significantly high DOC levels in wastewater effluent (Katsoyiannis and Samara, 2006, 2007) along with fast degradation of biodegradable DOC (~ 80% within 24 hours; Seidl et al., 1998) and residence time of Hooghly water (mentioned earlier), Samanta et al. (2015) suggested possibility of anthropogenic DOC biodegradation during its transport in the estuary. Although anthropogenic inputs were mostly confined to the freshwater regime, relatively higher DOC in the mixing regime of the Hooghly compared to the freshwater regime 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 the 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 that measures rates of groundwater and surface runoff mediated DOC additions is warranted.

Overall, on an average, the concentration of DOC in the Hooghly was ~ 40% higher than in the Sundarbans, which appeared to be due to cumulative effect of contributions from freshwater and groundwater, higher anthropogenic inputs, and DOC - POC interconversion. 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 this study was relatively higher than the range (Hooghly: 40.3 ± 1.1 to 129.7 ± 6.7 µM, Sundarbans: 45.4 ± 7.5 µM) reported by Ray et al. (2018) for the Hooghly-Sundarbans system. However, it was within the range (51 to 750 µM; Sarma et al., 2014) reported for a large set of Indian estuaries. No significant SPM - salinity or POC - salinity relationships were 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 regime 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 regime due to presence of several industries and large urban population (St: H2: Megacity Kolkata) that discharge industrial effluents and municipal wastewater to the estuary on regular basis (Table 1). A signal for surface runoff mediated POC addition was evident in the freshwater regime where ~ 61% and ~ 43% higher POC were observed at 'H3' and 'H4', respectively compared to an upstream location (St. H2). However, based on the present data, it was not possible to decouple freshwater and surface runoff mediated POC inputs to the Hooghly estuary. Relatively lower contribution of POC to the SPM pool of the Sundarbans (0.66 to 1.23%) compared to the Hooghly (0.96 to 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 ranges for $\delta^{13}C$ (rivers ~ – 28 to – 25‰; marine plankton ~ – 22 to – 18‰; C_3 plant ~ – 32 to – 24‰; C_4 plants ~ – 13 to –10‰; freshwater algae and their detritus ~ – 30 to – 40‰) have been reported in ecosystem (Smith and Epstein, 1971; Cerling et al., 1997; Bouillon et al., 2003; Bontes et al., 2006; Kohn, 2010; Marwick et al., 2015). 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 ($\delta^{13}C_{POC}$ ~ – 28 to – 14‰, Andrews et al., 1998; $\delta^{13}C_{DOC}$ ~ – 26‰, Jin et al., 2018). In the mixing regime 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 mangroves 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 to 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 has 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 regime (ΔPOC = – 0.45 to 0.48), whereas removal (n = 6) dominated over addition (n = 1) in the mixing regime (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 the adjacent continental shelf region, modification via conversion to DOC and degradation by respiration 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 regimes of the Hooghly estuary. Decrease in ΔPOC with increase in $\Delta\delta^{13}C_{POC}$ (n = 4 for the mixing regime and n = 1 for the freshwater regime) suggested degradation of POC by respiration. This process did not appear to significantly impact estuarine CO_2 pool as evident from the POC - pCO_2 relationship (freshwater regime: p = 0.29, mixing regime: p = 0.50; Fig. 5e). Decrease in both ΔPOC and $\Delta\delta^{13}C_{POC}$ (n = 2 for mixing regime and n = 2 for freshwater regime) supported settling of POC to sub-tidal sediment. Despite high water residence time, this process may not be effective in the Hooghly due to unstable estuarine condition (described earlier). Increase in ΔPOC with decrease in

$\Delta\delta^{13}C_{POC}$ (n = 2 for the freshwater regime) indicated POC inputs via surface and freshwater runoffs as well as phytoplankton productivity. Increase in both ΔPOC and $\Delta\delta^{13}C_{POC}$ (n = 1 for the mixing regime and n = 1 for the freshwater regime) may be linked to DOC to POC conversion by flocculation.

In the Sundarbans, negative and lower ΔPOC_{M2} (– 209 to – 28 µM) compared to ΔPOC_{M1} (– 35 to 327 µM) 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 degradation of POC by respiration 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 to 0.07 Tg and ~ 0.58 Tg annually for the Hooghly and Sundarbans, respectively (Ray et al., 2018).

4.4 pCO₂ and FCO₂ in the Hooghly-Sundarbans

The estimated pCO_2 for the Hooghly-Sundarbans system during this study were in the range (Cochin estuary: 150 to 3800 µatm, Gupta et al., 2009; Mandovi - Zuari estuary: 500 to 3500 µatm, Sarma et al., 2001) reported for other tidal estuaries of India. In the Sundarbans, barring three locations (S3, T3 and M2), a significant negative correlation between pCO_2 and % saturation of DO ($r^2 = 0.76$, p = 0.005; Figure not given) suggested presence of processes, such as degradation of OM by respiration, 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 OM degradation by respiration 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 [$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 18HCO_3^{2-} \rightarrow 124CO_2 + 140H_2O + 16NO_3^- + HPO_4^{2-}$; ΔCO_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 the 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 estuarine mangrove systems worldwide (Bouillon et al., 2007, Call et al., 2015, Rosentreter et al., 2018) suggested groundwater (or pore water) exchange to be a potential CO_2 source in such systems.

Unlike the Sundarbans, ECO_2 - AOU relationship did not confirm significant impact of OM degradation by respiration on CO_2 in either freshwater (p = 0.50) or mixing regimes (p = 0.75) of the Hooghly (Fig. 6c). Overall, pCO_2 in the freshwater regime of the Hooghly was significantly higher compared to the mixing regime (Table 3), which may be linked to additional CO_2 supply in the freshwater regime via freshwater or surface runoffs from adjoining areas (Table 1). Inter-estuary comparison of pCO_2 also revealed higher average pCO_2 in the Hooghly by ~ 1291 µatm compared to the Sundarbans, which was largely due to significantly higher pCO_2 in freshwater regime of the Hooghly (Table 2 & 3). Lack of negative correlation between pCO_2 - salinity in freshwater regime (Fig. 6d) of the Hooghly suggested limited contribution of CO_2 due to freshwater input. 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 perspectives, anthropogenically influenced Hooghly estuary was a relatively greater source of CO_2 to the regional atmosphere compared to the mangrove-dominated Sundarbans ($[FCO_2]_{Hooghly}$: $[FCO_2]_{Sundarbans}$ = 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 the mangrove-dominated estuaries (~ 43 to 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 the 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 cm hr^{-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.

5. 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. Considering different nature and quantity of supplied organic matter within these two contrasting systems, it was hypothesized in this study that C metabolism in these two estuaries was different with higher CO_2 exchange flux from the anthropogenically influenced estuary compared to the mangrove-dominated one. The results obtained during the study supported this hypothesis with significant differences in physicochemical parameters and active biogeochemical processes in these two estuaries. While freshwater intrusion along with inorganic and organic C metabolisms appeared to shape DIC dynamics in the Hooghly, significant DIC removal (via CO_2 outgassing, phytoplankton uptake as well as export to adjoining continental shelf region) and influence of groundwater were noticed in the Sundarbans. Relatively higher DOC concentration in the Hooghly compared to the Sundarbans was due to cumulative interactions among anthropogenic inputs, DOC-POC interconversion, and groundwater contribution. Freshwater runoff, terrestrial C_3 plants, and anthropogenic inputs contributed to POC pool in the Hooghly, whereas contribution from C_3 plants was dominant at the Sundarbans. Surface runoff from adjoining areas in the Hooghly and degradation of OM by respiration in the Sundarbans largely controlled pCO_2 in the system. Overall, 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 the Sundarbans, suggesting significant role played by anthropogenically stressed estuarine system from regional climate change perspective.

References

Abril, G., Nogueira, E., Hetcheber, H., Cabeçadas, G., Lemaire, E., and Brogueira, M.J.: Behaviour of organic carbon in nine contrasting European estuaries, Estuarine Coastal Shelf Sci., 54, 241–262, https://doi.org/10.1006/ecss.2001.0844, 2002.

Akhand, A., Chanda, A., Manna, S., Das, S., Hazra, S., Roy, R., Choudhury, S.B., Rao, K.H., Dadhwal, V.K., Chakraborty, K. and Mostofa, K.M.G.: A comparison of CO_2 dynamics and air-water fluxes in a river dominated estuary and a mangrove dominated marine estuary. Geophys. Res. Lett., 43(22), https://doi.org/10.1002/2016GL070716, 2016.

Akhand, A., Chandra, A., Dutta, S., and Hazra, S.: Air- water carbon dioxide exchange dynamics along the estuarine transition zone of Sunderban, northern Bay of Bengal, India, Indian J. Geo-Marine Sci. 41, 111–116, 2012.

Alongi, D.M., Ramanathan, A.L., Kannan, L., Tirendi, F., Trott, L.A., and Prasad, M.B.K.: Human induced disturbance on benthic microbial metabolism in the Pichavaram mangroves, Vellar Coleroon estuarine complex, India, Mar. Biol. 147, 1033-1044, https://doi.org/10.1007/s00227-005-1634-5, 2005.

Alling, V., Porcelli, D., Morth, C- M., Anderson, L. G., Sanchez- Garcia, L., Gustafsson, O., Andersson, P. S., and Humborg, C.: Degradation of terrestrial organic carbon, primary production and out-gassing of CO_2 in the Laptev and East Siberian Seas as inferred from $\delta^{13}C$ values of DIC, Geochim. Cosmochim. Acta, 95, 143–159, https://doi.org/10.1016/j.gca.2012.07.028, 2012.

Alongi, D.M.: Carbon cycling and storage in mangrove forests, Ann. Rev. Mar. Sci. 6, 195–219, 10.1146/annurev-marine-010213-135020, 2014.

Alongi, D.M., and Mukhopadhyay, S.K.: Contribution of mangroves to coastal carbon cycling in low latitude seas. Agric. For. Meteorol., 213, 266-272, doi:10.1016/j.agrformet.2014.10.005, 2014.

Andrews, J. E., Greenway, A.M., and Dennis, P.F.: Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary. Hunts Bay, Kingston Harbour, Jamaica, Estuar. Coast. Shelf Sci., 46, 743–456, https://doi.org/10.1006/ecss.1997.0305, 1998.

Barnes, J., Ramesh, R., Purvaja, R., Nirmal Rajkumar, A., Senthil Kumar, B., and Krithika, K.: Tidal dynamics and rainfall control N_2O and CH_4 emissions from a pristine mangrove creek, Geophys. Res. Lett. 33, L15405. doi:10.1029/ 2006GL026829, 2006.

Bauer, J. E., Cai, W.J., Raymond, P.A., Bianchi, T.S., Hopkinson, C.S., and Regnier, P.A.G.: The changing carbon cycle of the coastal ocean, Nature, 504 (7478), 61–70, doi: 10.1038/nature12857, 2013.

Bhavya, P.S., Kumar, S., Gupta, G.V.M., Sudharma, K.V., and Sudheesh, V.: Spatial-temporal variation in $\delta^{13}C_{DIC}$ of a tropical eutrophic estuary (Cochin estuary, India), Cont. **Shelf** Res. 153, 75-85, https://doi.org/10.1016/j.csr.2017.12.006, 2018.

Bhavya, P.S., Kumar, S., Gupta, G.V.M., and Sudheesh, V.: Carbon uptake rates in the Cochin estuary and adjoining coastal Arabian Sea, Estuaries and Coasts, 40, 447, doi: 10.1007/s12237-016-0147-4, 2017.

Biswas, H., Mukhopadhyay, S.K., Sen, S., and Jana, T.K.: Spatial and temporal patterns of methane dynamics in the tropical mangrove dominated estuary, NE Coast of Bay of Bengal, India. J. Marine Syst. 68, 55-64, https://doi.org/10.1016/j.jmarsys.2006.11.001, 2007.

Biswas, H., Mukhopadhyay, S. K., De, T. K., Sen, S., and Jana, T. K.: Biogenic controls on the air-water carbon dioxide exchange in the Sundarban mangrove environment, northeast coast of Bay of Bengal, India, Limnol. Oceanogr. 49, 95-101. doi: 10.4319/lo.2004.49.1.0095, 2004.

Borges, A. V., Delille, B., and Frankignoulle, M.: Budgeting sinks and sources of CO_2 in the coastal ocean: Diversity of ecosystems counts, Geophys. Res. Lett., 32, L14601, https://doi.org/10.1029/2005gl023053, 2005.

Borges, A. V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G., and Frankignoulle, M.: Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt and Thames), Limnol. Oceanogr., 49, 1630–1641, https://doi.org/10.4319/lo.2004.49.5.1630, 2004.

Bouillon, S., Borges, A. V., Castañeda-Moya, E., Diele, K., Dittmar, T., Duke, N. C., Kristensen, E., Lee, S. Y., Marchand, C., Middelburg, J. J., Rivera-Monroy, V. H., Smith, T. J., and Twilley, R. R.: Mangrove production and carbon sinks: A revision of global budget estimates, Global Biogeochem. Cy., 22, GB2013, 10.1029/2007GB003052, 2008.

Bouillon, S., Dehairs, F., Velimirov, B., Abril, G., and Borges, A.V.: Dynamics of organic and inorganic carbon across contiguous mangrove and seagrass systems (Gazi Bay, Kenya), J. Geophys. Res., 112, G02018, doi:10.1029/2006JG000325, 2007.

Bouillon, S., Korntheuer, M., Baeyens, W., and Dehairs, F.: A new automated setup for stable isotope analysis of dissolved organic carbon. Limnol. Oceanogr.; Methods 4, 216. doi: 10.4319/lom.2006.4.216, 2006.

Bouillon. S., Frankignoulle, M., Dehairs, F., Velimirov, B., Eiler, A., Etcheber, H., Abril, G., and Borges, A.V.: Inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra Pradesh, India) during pre-monsoon: the local impact of extensive mangrove forests, Global Biogeochem. Cy. 17 (4), 1114, doi:10.1029/ 2002GB00202, 2003.

Boto, K. G., and Wellington, J.T.: Seasonal variations in concentrations and fluxes of dissolved organic and inorganic materials in a tropical, tidally dominated waterway, Mar. Ecol. Prog. Ser., 50, 151–160, 1988.

Bontes, B., Pel, R., Ibelings, B.W., Boscker, H.T.S., Middelburg, J.J., and Donk, E,V.: The effects of biomanipulation on the biogeochemistry, carbon isotopic composition and pelagic food web relations of a shallow lake, Biogeosciences, 3, 69 - 83, Biogeosciences, 3, 69 - 83, www.biogeosciences.net/3/69/2006/, 2006.

Call, M., Maher, D.T., Santos, I.R., Ruiz-Halpern, S., Mangion, P., and Sanders, et al.: Spatial and temporal variability of carbon dioxide and methane fluxes over semidiurnal and spring–neap–spring timescales in a mangrove creek. Geochim. Cosmochim. Acta, 150, 211–225, https://doi.org/10.1016/j.gca.2014.11.023, 2015.

Cai, W.-J.: Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration?, Annu. Rev. Mar. Sci., 3, 123–145, https://doi.org/10.1146/annurev-marine120709-142723, 2011.

Cai, W.-J., Dai, M., and Wang, Y.: Air-sea exchange of carbon dioxide in ocean margins: A province-based synthesis, Geophys. Res. Lett., 33, 2–5, 2006.

Cai, W.-J., Wang, Y., Krest, J., and Moore, W.S.: The geochemistry of dissolved inorganic carbon in a surficial groundwater aquifer in North Inlet, South Carolina and the carbon fluxes to the coastal ocean, Geochim. Cosmochim. Acta, 67, 631–637, https://doi.org/10.1016/S0016-7037(02)01167-5, 2003.

Carpenter, I.H., Bradford, W.L., and Grant, V.: Processes affecting the composition of estuarine waters. In: Cronin, L.E. (Ed.), Estuarine Research. 1. Academic, pp. 188–214, 1975.

Camilleri, J. C., and Ribi, G.: Leaching of dissolved organic carbon (DOC) from dead leaves, formation of flakes from DOC, and feeding on flakes by crustaceans in mangroves, Mar. Biol., 91, 337– 344, 1986.

Cerling, T. E., Harris, J.H., MacFadden, B.J., Leakey, M.G., Quadek, J., Eisenmann, V., and Ehleringer, J.R.: Global vegetation change through the Miocene/Pliocene boundary, Nature, 389, 153–158, https://doi.org/10.1038/38229, 1997.

Chen, C.-T. A. and Borges, A. V.: Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO_2, Deep-Sea. Res. Pt. II., 56, 578–590, 2009.

CIFRI,: Present status of Hilsa in Hooghly – Bhagirathi river, Central Inland Fisheries Research Institute. www.cifri.ernet.in/179.pdf, 2012.

Cotovicz Jr., L. C., Knoppers, B. A., Brandini, N., Costa Santos, S. J., and Abril, G.: A strong CO_2 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil), Biogeosciences, 12, 6125-6146, https://doi.org/10.5194/bg-12-6125-2015, 2015.

Dittmar, T., Hertkorn, N., Kattner, G., and Lara, R. J.: Mangroves, a major source of dissolved organic carbon to the oceans, Global Biogeochem. Cycles, 20, doi:10.1029/ 2005gb002570, 2006.

Dittmar, T., and Lara, R.J.: Driving forces behind nutrient and organic matter dynamics in a mangrove tidal creek in north Brazil, Estuarine Coastal Shelf Sci., 52, 249 – 259, https://doi.org/10.1006/ecss.2000.0743, 2001.

Donato, D.C., Kauffman, J.B., Kurnianto, S., Stidham, M., and Murdiyarso, D.: Mangroves among the most carbon-rich forests in the tropics. Nat. Geosci., 4, 293-297, doi: 10.1038/NGEO1123, 2011.

Dutta, K., Ravi Prasad, G. V., Ray, D. K., and Raghav, K.: Decadal changes of Radiocarbon in the surface Bay of Bengal: Three decades after GEOSECS and one decade after WOCE, Radiocarbon, 52(2–3), 1191–1196, 2010.

Dutta, M.K., Bianchi, T.S., and Mukhopadhyay, S.K.: Mangrove methane biogeochemistry in the Indian Sundarbans: a proposed budget, Frontiers in Marine Science, 4, 187. doi: 10.3389/fmars.2017.00187, 2017.

Dutta, M. K., Mukherkjee, R., Jana, T. K., and Mukhopadhyay, S. K.: Biogeochemical dynamics of exogenous methane in an estuary associated to a mangrove biosphere; the Sundarbans, NE coast of India, Mar. Chem. 170, 1–10, doi: 10.1016/j.marchem.2014.12.006, 2015.

Dutta, M. K., Chowdhury, C., Jana, T. K., and Mukhopadhyay, S. K.: Dynamics and exchange fluxes of methane in the estuarine mangrove environment of Sundarbans, NE coast of India, Atmos. Environ. 77, 631–639, doi: 10.1016/j.atmosenv.2013.05.050, 2013.

Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E., and Théate, J.-M.: Carbon dioxide emission from European estuaries, Science, 282, 434–436, https://doi.org/10.1126/science.282.5388.434, 1998.

Frankignoulle, M., and Borges, A. V.: Direct and indirect $p\mathrm{CO_2}$ measurements in a wide range of $p\mathrm{CO_2}$ and salinity values (the Scheldt estuary), Aquat. Geochem. 7, 267 - 273. doi: 10.1023/A:1015251010481, 2001.

Fry, B.: Conservative mixing of stable isotopes across estuarine salinity gradients: a conceptual framework for monitoring watershed influences on downstream fisheries production, Estuaries 25, 264–271, https://doi.org/10.1007/BF02691313, 2002.

Freitas, H.A., Pessenda, L.C.R., Aravena, R., Gouveia, S.E.M., Ribeiro, A.S., and Boulet, R.: Late quaternary vegetation dynamics in the southern Amazon Basin inferred from carbon isotopes in soil organic matter. Quat. Res. 55, 39–46, https://doi.org/10.1006/qres.2000.2192 2001.

Ganguly, D., Dey, M., Sen, S., and Jana, T.K.: Biosphere-atmosphere exchange of NOx in the tropical mangrove forest, J. Geophys. Res. 114, G04014. http:// dx.doi.org/10.1029/2008JG000852, 2009.

Ganguly, D., Dey, M., Mandal, S.K., De, T.K., and Jana, T.K.: Energy dynamics and its implication to biosphere-atmosphere exchange of CO_2, H_2O and CH_4 in a tropical mangrove forest canopy, Atmos. Environ. 42, 4172 – 4184, 2008.

Gattuso, J.-P., Frankignoulle, M., Bourge, I., Romaine, S., and Buddemeier, R. W.: Effect of calcium carbonate saturation of seawater on coral calcification, Glob. Planet. Change, 18,37-46, https://doi.org/10.1016/S0921-8181(98)00035-6, 1998.

Ghosh, B, B., Ray, P., and Gopalakrishnan, V.: Survey and characterization of waste water discharged into the Hooghly Estuary, J. Inland Fishery Soc. of India, 4, 2–10, 1973.

Giri, C., Ochieng, E., Tieszen, L., Zhu, Z., Singh, A., Loveland, T., Masek, J., and Duke, N.: Status and distribution of mangrove forests of the world using earth observation satellite data. Global Ecol. Biogeogr. 20(1), 154-159, 2011.

Goutam, K.S., Tanaya, D., Anwesha, S., Sharanya, C., and Meenakshi, C.: Tide and mixing characteristics in Sundarbans Estuarine River system, Hydrol. Current Res. 6 (2), https://doi.org/10.4172/2157-7587.1000204, 2015.

Grasshoff, K., Ehrharft,M., and Kremling, K.: .Methods of Seawater Analysis, 2nd Edn.Weinheim: Verlag Chemie, 1983.

Guo, X., Dai, M., Zhai, W., Cai, W.-J., and Chen, B.: CO_2 flux and seasonal variability in a large subtropical estuarine system, the Pearl River Estuary, China. J. Geophys. Res. 114, G03013. http://dx.doi.org/10.1029/2008JG000905, 2009.

Gupta, G.V.M., Thottathil, S.D., Balachandran, K.K., Madhu, N.V., Madeswaran, P., and Nair, S.: CO_2 supersaturation and net heterotrophy in a tropical estuary (Cochin, India): influence of anthropogenic effect, Ecosystems, 12 (7), 1145-1157, https://doi.org/10.1007/s10021-009-9280-2, 2009.

Heip, C. H. R., Goosen, N.K., Herman, P.M.J., Kromkamp, J., Middelburg, J.J., and Soetaert, K.: Production and consumption of biological particles in temperate tidal estuaries, Oceanogr. Mar. Biol. Annu. Rev., 33, 1–149, 1995.

Hopkinson, C.S., Fry, B., Nolin, A.: Stoichiometry of dissolved organic matter dynamics on the continental shelf of the Northeastern USA, Cont. Shelf Res. 17, 473–489, doi: 10.1016/S0278-4343(96)00046-5, 1997.

Huang T.-H., Fu Y.-H., Pan P.-Y., Arthur Chen, C.-T.: Fluvial carbon fluxes in tropical rivers, Curr. Opin. Environ. Sustain. 4, 162–169, https://doi.org/10.1016/j.cosust.2012.02.004, 2012.

Ittekkot, V., and Laane, R.W.P.M.: Fate of riverine particulate organic matter. In: Degens, E.T.; Kemp, S.; Richey, J.E., eds. Biogeochemistry of major world rivers. Chichester: Wiley; 233-243, 1991.

Ittekkot, V.: Global trends in the nature of organic matter in river suspensions, Nature 332, 436–438, 1988.

Jennerjahn, T., and Ittekkot, C. V.: Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil: I. Amino acids and hexosamines, Oceanol. Acta 20, 359–369, 1997.

Jin, H., Yoon, T.K., Begum, M.S., Lee, E.J., Oh, N.H., Kang, N., and Park, J.H.: Longitudinal discontinuities in riverine greenhouse gas dynamics generated by dams and urban wastewater, Biogeosciences, 15, 6349 - 6369, https://doi.org/10.5194/bg-15-6349-2018, 2018.

Katsoyiannis A. and Samara C.: The Fate of Dissolved Organic Carbon (DOC) in the wastewater treatment process and its importance in the removal of wastewater contaminants, Environ. Sci. Pollut. Res. 14, 284–292, https://doi.org/10.1065/espr2006.05.302, 2007.

Katsoyiannis A. and Samara C.: Ecotoxicological evaluation of the wastewater treatment process of the sewage treatment plant of Thessaloniki, Greece, J. Hazard. Mater. 141, 614–621, https://doi.org/10.1016/j.jhazmat.2006.07.038, 2006.

Khan, R. A.: The pollution problem of Hooghly estuarine system; Estuarine Ecosystem Series, Zoological survey of India, part 2, 497–542, 1995.

Kohn, M. J.: Carbon isotope compositions of terrestrial C_3 plants as indicators of (paleo) ecology and (paleo) climate, Proc. Natl. Acad. Sci. U.S.A., 107, 19691–19695, 2010.

Kristensen, E., and Alongi, D.M.: Control by fiddler crabs (Ucavocans) and plant roots (Avicennia marina) on carbon, iron, and sulphur biogeochemistry in mangrove sediment, Limnol. Oceanogr. 51, 1557–1571, doi: 10.4319/lo.2006.51.4.1557, 2006.

Kristensen, E., and Suraswadi, P.: Carbon, nitrogen and phosphorus dynamics in creek water of a Southeast Asian mangrove forest, Hydrobiologia, 474, 197–211, 2002.

Le Quéré, C., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Peters, G. P., Manning, A. C., Boden, T. A., Tans, P. P., Houghton, R. A., Keeling, R. F., Alin, S., Andrews, O. D., Anthoni, P., Barbero, L., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P., Currie, K., Delire, C., Doney, S. C., Friedlingstein, P., Gkritzalis, T., Harris, I., Hauck, J., Haverd, V., Hoppema, M., Klein Goldewijk, K., Jain, A. K., Kato, E., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lombardozzi, D., Melton, J. R., Metzl, N., Millero, F., Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., O'Brien, K., Olsen, A., Omar, A. M., Ono, T., Pierrot, D., Poulter, B., Rödenbeck, C., Salisbury, J., Schuster, U., Schwinger, J., Séférian, R., Skjelvan, I., Stocker, B. D., Sutton, A. J., Takahashi, T., Tian, H., Tilbrook, B., van der Laan-Luijkx, I. T., van der Werf, G. R., Viovy, N., Walker, A. P., Wiltshire, A. J., and Zaehle, S.: Global Carbon Budget 2016, Earth Syst. Sci. Data, 8, 605–649, https://doi.org/10.5194/essd-8-605-2016, 2016.

Linto N., Barnes, J., Ramachandran, R., Divia, J., Ramachandran, P., and Upstill-Goddard, R. C.: Carbon dioxide and methane emissions from mangrove-associated waters of the Andaman Islands, Bay of Bengal, Estuaries and Coasts, 37, 381–398, https://doi.org/10.1007/s12237-013-9674-4, 2014.

Liss, P. S., and Merlivat, L.: "Air sea gas exchange rates: introduction and synthesis," in The Role of Air Sea Exchange in Geochemical Cycling, ed P. Buat-Menard (Hingham, MA: D. Reidel) 113–129, 1986.

Maher, D., Santos, I., Golsby-Smith, L., Gleeson, J., and Eyre, B.: Groundwater-derived dissolved inorganic and organic carbon exports from a mangrove tidal creek: The missing mangrove carbon sink?, Limnol. Oceanog., 58, 475–488, doi:10.4319/lo.2013.58.2.0475, 2013.

Marwick, T. R., Tamooh, F., Teodoru, C.R., Borges, A.V., Darchambeau, F., and Bouillon, S.: The age of river-transported carbon: A global perspective, Global Biogeochem. Cycles, 29, 122–137, doi:10.1002/ 2014GB004911, 2015.

Millero, F.J.: Chemical Oceanography, Fourth Edition, CRC press, Taylor and Francis Group, 2013.

Miyajima T., Tsuboi Y., Tanaka Y., and Koike, I.: Export of inorganic carbon from two Southeast Asian mangrove forests to adjacent estuaries as estimated by the stable isotope composition of dissolved inorganic carbon, J. Geophys. Res., 114, G01024, doi:10.1029/2008JG000861, 2009.

Moran, M.A., Sheldon Jr., W.M., and Sheldon, J.E.: Biodegradation of riverine dissolved organic carbon in five estuaries of the south United States, Estuaries 22, 55 – 64, 1999.

Mook,W.G., and Tan, T.C.: Stable carbon isotopes in rivers and estuaries. In: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), Biogeochemistry of Major World Rivers. SCOPE, John Wiley and Sons Ltd., pp. 245–264, 1991.

Mukhopadhyay, S.K., Biswas, H., De, T.K., and Jana, T.K.: Fluxes of nutrients from the tropical river Hooghly at the land-ocean boundary of Sundarbans, NE coast of Bay of Bengal, India, J. Marine Syst. 62 (1-2), 9-21, https://doi.org/10.1016/j.jmarsys.2006.03.004, 2006.

Mukhopadhyay, S.K., Biswas, H., De, T.K., Sen, S., and Jana, T.K.: Seasonal effects on the air–water carbon dioxide exchange in the Hooghly estuary, NE coast of Bay of Bengal, India, J Environ Monit. 36 (4), 629-638, 10.1039/b201614a, 2002.

Ray, R., Baum, A., Rixen, T., Gleixner, G., and Jana, T.K.: Exportation of dissolved (inorganic and organic) and particulate carbon from mangroves and its implication to the carbon budget in the Indian Sundarbans, Sci. Total Environ., 621, 535-547. https://doi.org/10.1016/j.scitotenv.2017.11.225, 2018.

Ray, R., Rixen, T., Baum, A., Malik, A., Gleixner, G., and Jana, T.K.: Distribution, sources and biogeochemistry of organic matter in a mangrove dominated estuarine system (Indian Sundarbans) during the pre-monsoon, Estuar. Coast. Shelf Sci. 167, 404–413, http://dx.doi.org/10.1016/j.ecss.2015.10.017, 2015.

Ray, R., Ganguly, D., Chowdhury, C., Dey, M., Das, S., Dutta, M.K., Mandal, S.K., Majumder, N., De, T.K., Mukhopadhyay, S.K., and Jana, T.K.: Carbon sequestration and annual increase of carbon stock in a mangrove forest, Atmos. Environ. 45, 5016-5024, https://doi.org/10.1016/j.atmosenv.2011.04.074, 2011.

Raymond, P. A. and Cole, J. J.: Gas exchange in rivers and estuaries: Choosing a gas transfer velocity, Estuaries, 24, 312–317, https://doi.org/10.2307/1352954, 2001.

Raymond, P.A., Bauer, J.E.: DOC cycling in a temperate estuary: a mass balance approach using natural ^{14}C and ^{13}C, Limnol. Oceanogr. 46, https://doi.org/10.4319/lo.2001.46.3.0655, 655-667, 2001.

Reay, W.G., Gallagher, D., and Simmons, G.M.: 1995. Sediment water column nutrient exchanges in Southern Chesapeake Bay near shore environments, Virginia Water Resources Research Centre, Bulletin - 181b, 1995.

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., Laruelle, G. G., Lauerwald, R., Luyssaert, S., Andersson, A. J., Arndt, S., Arnosti, C., Borges, A. V., Dale, A. W., Gallego-Sala, A., Godderis, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRowe, D. E., Leifeld, J., Meysman, F. J. R., Munhoven, G., Raymond, P. A., Spahni, R., Suntharalingam, P., and Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean, Nat. Geosci., 6, 597–607, doi:10.1038/ngeo1830, 2013.

Rosentreter, J.A., Maher, D.T., Erler, D.V., Murray, R. and Eyre, B.D.: Seasonal and temporal CO_2 dynamics in three tropical mangrove creeks - A revision of global mangrove CO_2 emissions. Geochim. Cosmochim. Acta, 222, 729-745, https://doi.org/10.1016/j.gca.2017.11.026, 2018.

Rudra, K.: Changing river courses in the western part of the ganga-Brahmaputra delta. Geomorphology 227, 87–100, doi: 10.1016/j.geomorph.2014.05.013, 2014.

Sadhuram, Y., Sarma, V.V., Ramana Murthy, T.V. and Prabhakara Rao, B.: Seasonal variability of physicochemical characteristics of the Haldia channel of Hooghly estuary, India. J. Earth Syst. Sci.., 114, 37–49, https://doi.org/10.1007/BF02702007, 2005.

Samanta, S., Dalai, T.K.: Massive production of heavy metals in the Ganga (Hooghly) River Estuary, India: global importance of solute-particle interaction and enhanced metal fluxes to the oceans, Geochim. Cosmochim. Acta, 228, 243–258, https://doi.org/10.1016/j.gca.2018.03.002, 2018.

Samanta, S., Dalai, T. K., Pattanaik, J. K., Rai, S. K., and Mazumdar, A.: Dissolved inorganic carbon (DIC) and its $\delta^{13}C$ in the Ganga (Hooghly) River estuary, India: Evidence of DIC generation via organic carbon degradation and carbonate dissolution, Geochim. Cosmochim. Acta, 165, 226 – 248, doi: 10.1016/j.gca.2015.05.040, 2015.

Sarkar, S.K., Mondal, P., Ok, Y.S., Rinklebe, J.: Trace metal in surface sediments of the Hooghly (Ganges) estuary: distribution and contamination risk assessment, Environ. Geochem. Health 39 (6), 1245–1258, DOI: 10.1007/s10653-017-9952-3, 2017.

Sarma, V.V.S.S., Krishna, M.S., Prasad, V.R., Kumar, B.S.K., Naidu, S.A., Rao, G.D., Viswanadham, R., Sridevi, T., Kumar, P.P., and Reddy, N.P.C.: Sources and transformation of particulate organic matter in the Indian monsoonal estuaries during discharge period, J. Geophys. Res.: Biogeosci..119(11), 2095 – 2111, https://doi.org/10.1029/2011GL050709, 2014.

Sarma, V.V.S.S., Viswanadham, R., Rao, G.D., Prasad, V.R., Kumar, B.S.K., Naidu, S.A., Kumar, N.A., D.B. Rao, Sridevi, T., Krishna, M.S., Reddy, N.P.C., Sadhuram, Y., and Murty, T.V.R.: Carbon dioxide emissions from Indian monsoonal Estuaries. Geophys. Res. Lett. 39, L03602, doi:10.1029/ 2011GL050709, 2012.

Sarma, V.V.S.S., Kumar, M.D., and Manerikar, M.: Emission of carbon dioxide from a tropical estuarine system, Goa, India, Geophys. Res. Lettrs., 28, 1239-1242, https://doi.org/10.1029/2000GL006114, 2001.

Servais, P., Billen, G., and Hascoet, M.C.: Determination of the biodegradable fraction of dissolved organic matter in waters, Water Res. 21,445 – 50, https://doi.org/10.1016/0043-1354(87)90192-8, 1987.

Seidl, M., Servais, P., and Mouchel, J. M.: Organic matter transport and degradation in the river Seine (France) after a combined sewer overflow, Water Res. 32, 3569–3580, https://doi.org/10.1016/S0043-1354(98)00169-9, 1998.

Somayajulu B. L. K., Rengarajan R., and Jani R. A.: Geochemical cycling in the Hooghly estuary, India. Mar. Chem., 79, 171–183. DOI: 10.1016/S0304-4203(02)00062-2, 2002.

Smith, B.N., and Epstein, S.: Two categories of $^{13}C/^{12}C$ ratios for higher plants, Plant Physiology, 47, 380 - 384. https://doi.org/10.1104/pp.47.3.380, 1971.

Sippo, J. Z., Maher, D. T., Tait, D. R., Holloway, C., and Santos, I. R.: Are mangroves drivers or buffers of coastal acidification? Insights from alkalinity and dissolved inorganic carbon export estimates across a latitudinal transect, Global Biogeochem. Cy., 30, 753–766. doi:10.1002/2015GB005324, 2016.

Singh, G., Ramanathan, A.L., Santra, S.C., Rajan, R.K.: Tidal control on the nutrient variability in Sundarban mangrove ecosystem, Journal of Applied Geochemistry, 18(4), 495-503, 2016.

Tait, D. R., Maher, D. T., Macklin, P. A., and Santos, I. R.: Mangrove pore water exchange across a latitudinal gradient, Geophys. Res. Lett. 43, 3334–3341. doi: 10.1002/2016GL068289, 2016.

Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, J. Geophys. Res., 97, 7373–7382, https://doi.org/10.1029/92JC00188, 1992.

Weiss, R.F.: The solubility of nitrogen, oxygen and argon in water and seawater, Deep Sea Research and Oceanographic Abstracts, 17(4), 721-735, https://doi.org/10.1016/0011-7471(70)90037-9, 1970.

Zhai, W., Dai, M., and Guo, X.: Carbonate system and CO_2 degassing fluxes in the inner estuary of Changjiang (Yangtze) River, China, Mar. Chem., 107, 342–356, https://doi.org/10.1016/j.marchem.2007.02.011, 2007.

Zhai, W.D., Dai, M.H., Cai, W.J., Wang, Y.C., and Wang. Z.H.: High partial pressure of CO_2 and its maintaining mechanism in a subtropical estuary: The Pearl River estuary, China. Mar. Chem. 93(1): 21 - 32. https://doi.org/10.1016/j.marchem.2004.07.003, 2005.

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

Parameters	**Hooghly**	**Sundarbans**
Nutrients (postmonsoon)	DIN: 14.72 ± 1.77 to 27.20 ± 2.05 μM DIP: 1.64 ± 0.23 to 2.11 ± 0.46 μM DSi: 77.75 ± 6.57 to 117.38 ± 11.54 μM (Mukhopadhyay et al., 2006)	DIN: 11.70 ± 7.65 μM DIP: 1.01 ± 0.52 μM DSi: 75.9 ± 36.9 μM (Biswas et al., 2004)
Chl *a* (postmonsoon)	2.35 - 2.79 mg m^{-3} (Mukhopadhyay et al., 2006)	7.88 ± 1.90 mg m^{-3} (Dutta et al., 2015)
Population density	North 24 Parganas and Hooghly: 2500 km^{-2}, Kolkata: 22000 km^{-2}, Howrah: 3300 km^{-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	6×10^4 km^2 (Sarkar et al., 2017)	No information available
Industrial and municipal wastewater discharge	1153.8 million 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 flux across water-atmosphere interface at the estuaries of Sundarbans. Here, W_T = water temperature, DO = dissolved oxygen.

Station	W_T (ºC)	Salinity	DO (mgL^{-1})	pH	DIC (μM)	$\delta^{13}C_{DIC}$ (‰)	DOC (μM)	POC (μM)	$\delta^{13}C_{POC}$ (‰)	pCO_2 (μatm)	FCO_2 ($\mu mol\ m^{-2}\ hr^{-1}$)
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 flux across water-atmosphere interface at the Hooghly estuary. Here, W_T = water temperature, DO = dissolved oxygen.

Station	W_T (ºC)	Salinity	DO (mgL^{-1})	pH	DIC (μM)	$\delta^{13}C_{DIC}$ (‰)	DOC (μM)	POC (μM)	$\delta^{13}C_{POC}$ (‰)	pCO_2 (μatm)	FCO_2 (μmol m^{-2} hr^{-1})
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 the Hooghly-Sundarbans system.

Ecosystems	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

Figure Captions:

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

Fig. 2: % saturation of DO - salinity relationship in the Hooghly-Sundarbans system.

Fig. 3: (a) DIC - salinity in the Hooghly, (b) $\delta^{13}C_{DIC}$ - salinity in the Hooghly, (c) ΔDIC - Δ $\delta^{13}C_{DIC}$ in the Hooghly, (d) DIC - salinity in the Sundarbans, and (e) $\delta^{13}C_{DIC}$ - salinity in the Sundarbans.

Fig. 4: (a) DOC - salinity in the Hooghly-Sundarbans system, (b) DOC - pCO_2 in the Hooghly, (c) DOC - pCO_2 in the Sundarbans, and (d) DOC - POC in the Hooghly-Sundarbans system.

Fig. 5: (a) SPM - salinity in the Hooghly-Sundarbans system, (b) POC - salinity in the Hooghly-Sundarbans system, (c) %POC/SPM - salinity in the Hooghly-Sundarbans system, (d) ΔPOC - Δ $\delta^{13}C_{POC}$ in the Hooghly, (e) POC - pCO_2 in the Hooghly, and (f) POC - pCO_2 in the Sundarbans.

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.

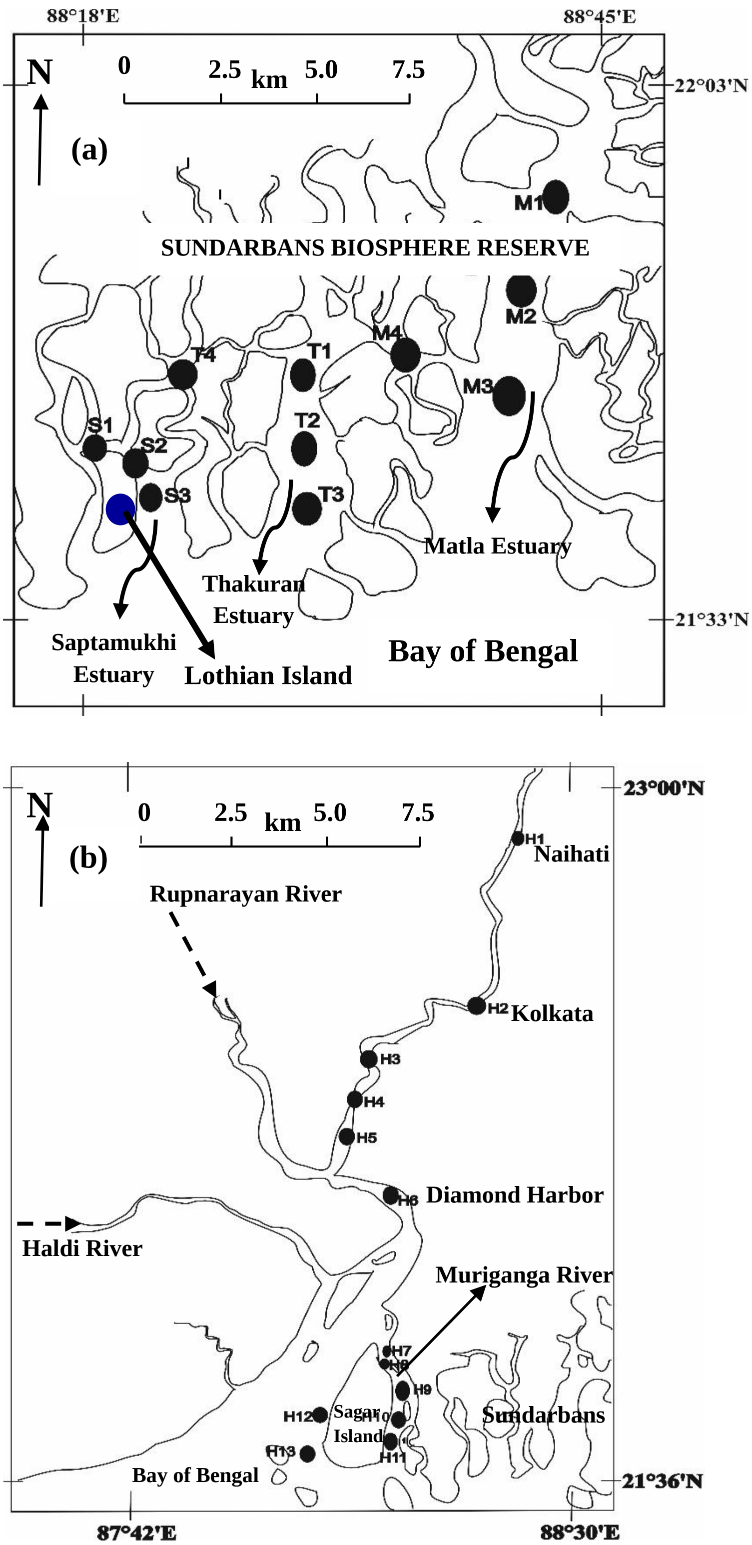
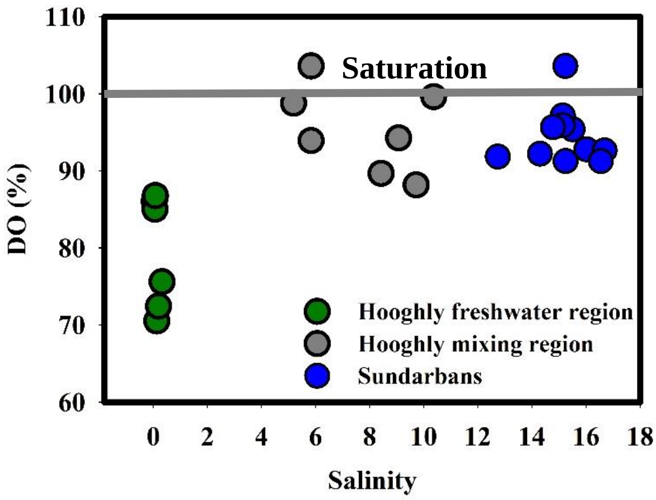

88°18'E
88°45'E
22°03'N
21°33'N
N
0
2.5
km
5.0
7.5
(a)
M1
SUNDARBANS BIOSPHERE RESERVE
M2
M4
T4
T1
M3
S1
S2
T2
S3
T3
Matla Estuary
Thakuran
Estuary
Saptamukhi
Estuary
Lothian Island
Bay of Bengal
23°00'N
N
0
2.5
km
5.0
7.5
(b)
H1
Naihati
Rupnarayan River
H2
Kolkata
H3
H4
H5
Diamond Harbor
Haldi River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

Fig. 1



Saturation
DO (%)
Salinity
Hooghly freshwater region
Hooghly mixing region
Sundarbans
110
100
90
80
70
60
0 2 4 6 8 10 12 14 16 18

Fig. 2

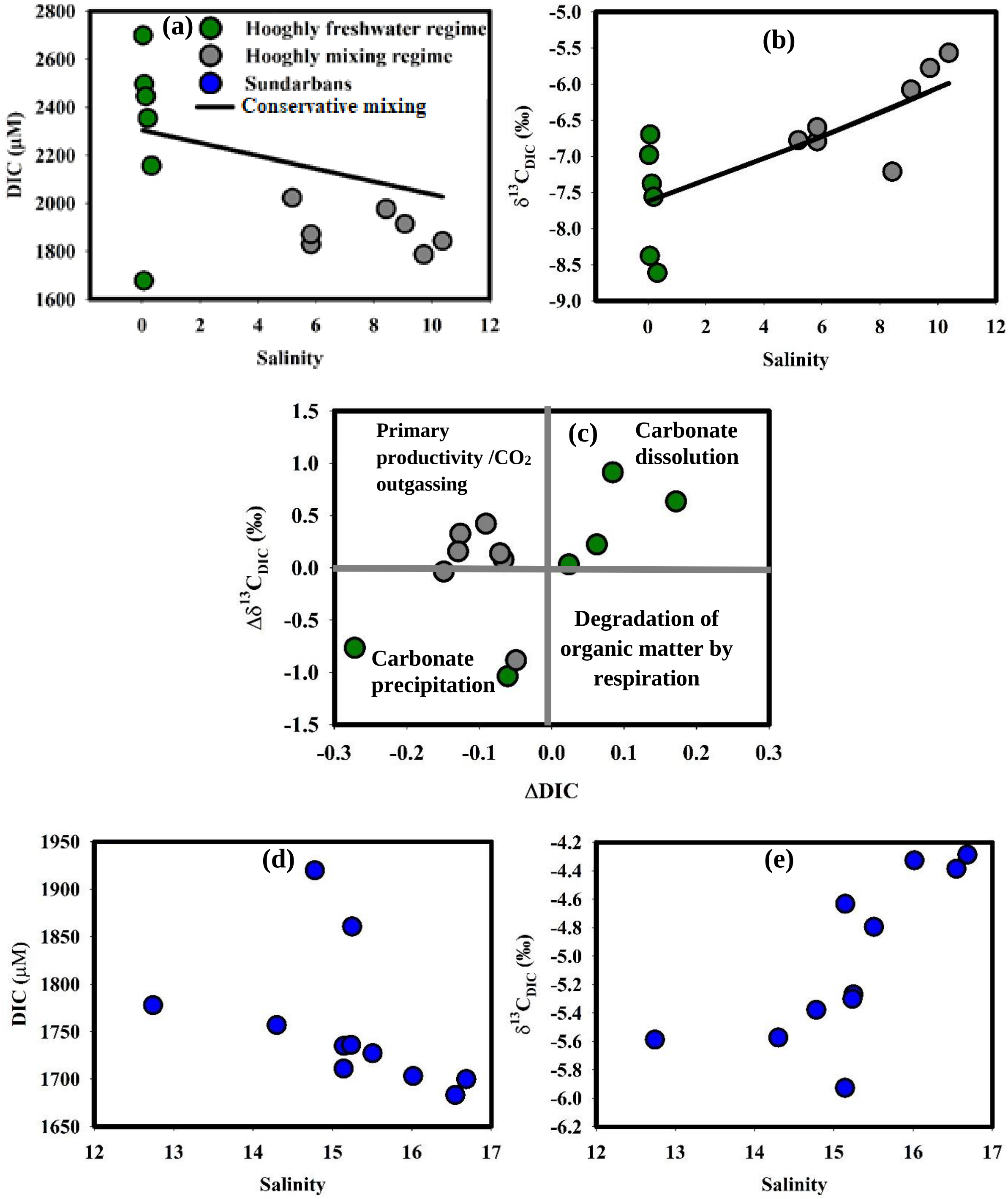

(a)
Hooghly freshwater regime
Hooghly mixing regime
Sundarbans
Conservative mixing
DIC (μM)
Salinity
(b)
δ13CDIC (‰)
Salinity
(c)
Primary productivity /CO2 outgassing
Carbonate dissolution
Carbonate precipitation
Degradation of organic matter by respiration
Δδ13CDIC (‰)
ΔDIC
(d)
DIC (μM)
Salinity
(e)
δ13CDIC (‰)
Salinity

Fig. 3

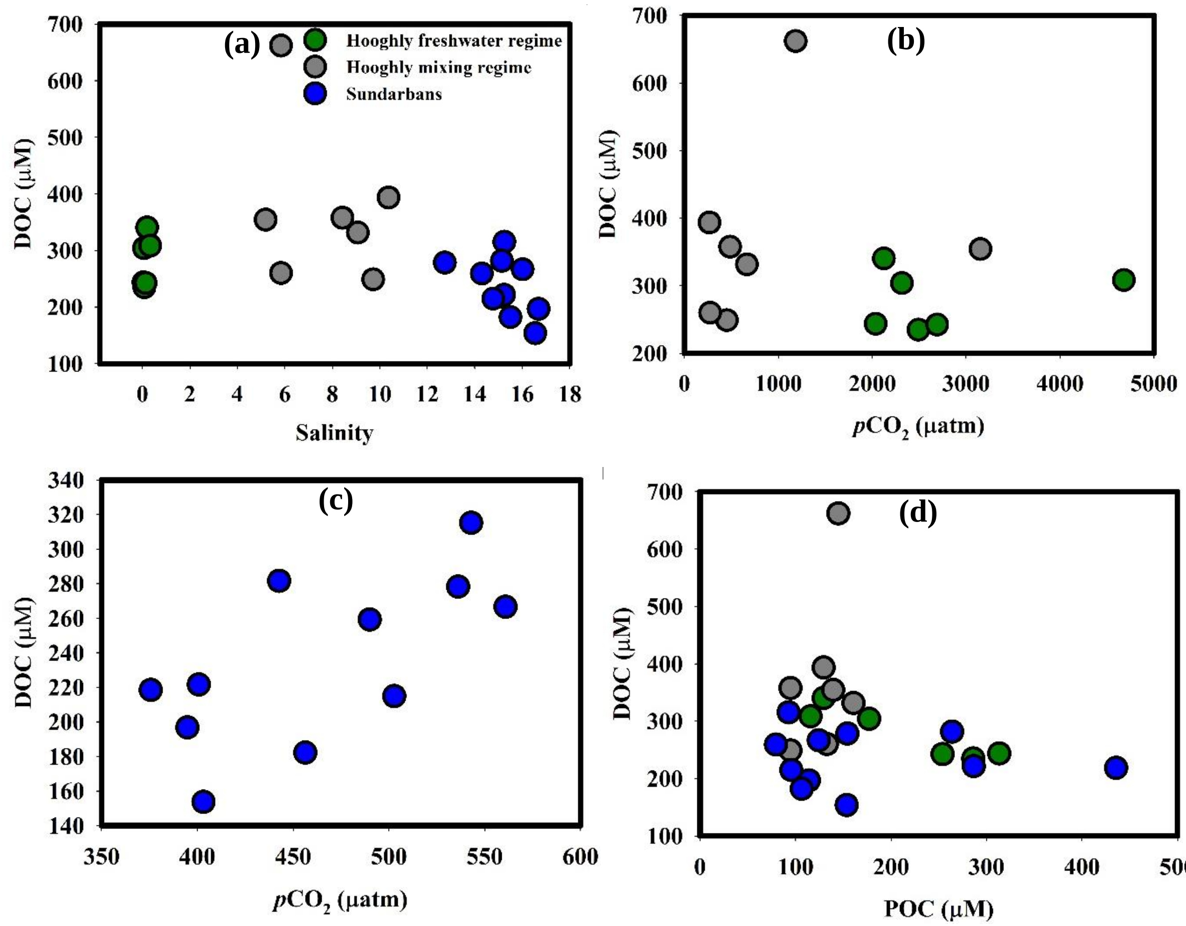
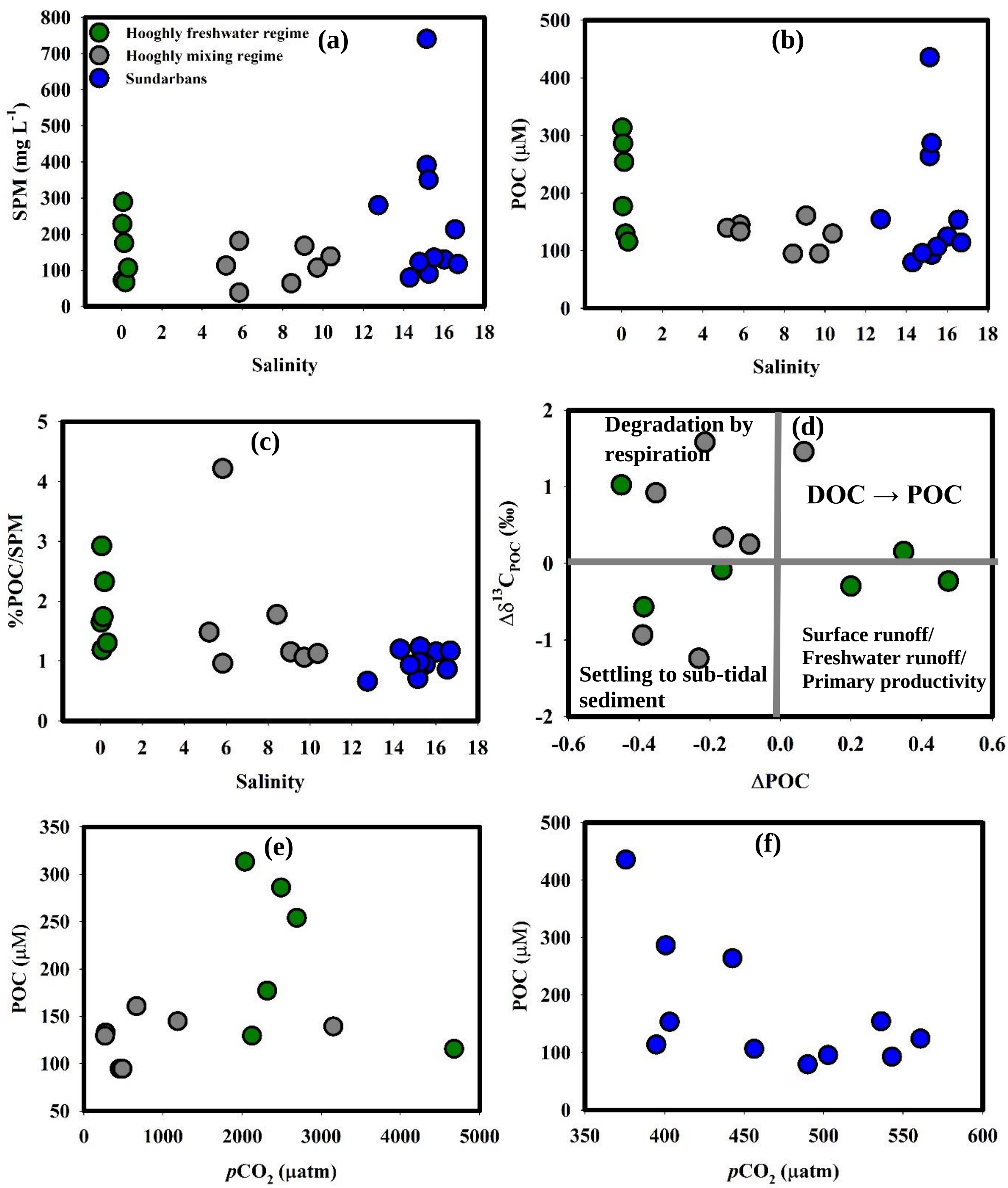

(a)
Hooghly freshwater regime
Hooghly mixing regime
Sundarbans
DOC (μM)
Salinity
(b)
DOC (μM)
pCO2 (μatm)
(c)
DOC (μM)
pCO2 (μatm)
(d)
DOC (μM)
POC (μM)

Fig. 4



(a)
Hooghly freshwater regime
Hooghly mixing regime
Sundarbans
SPM (mg L^{-1})
Salinity
(b)
POC (µM)
Salinity
(c)
%POC/SPM
Salinity
(d)
Degradation by respiration
DOC → POC
Settling to sub-tidal sediment
Surface runoff/ Freshwater runoff/ Primary productivity
$\Delta\delta^{13}C_{POC}$ (‰)
ΔPOC
(e)
POC (µM)
pCO$_2$ (µatm)
(f)
POC (µM)
pCO$_2$ (µatm)

Fig. 5

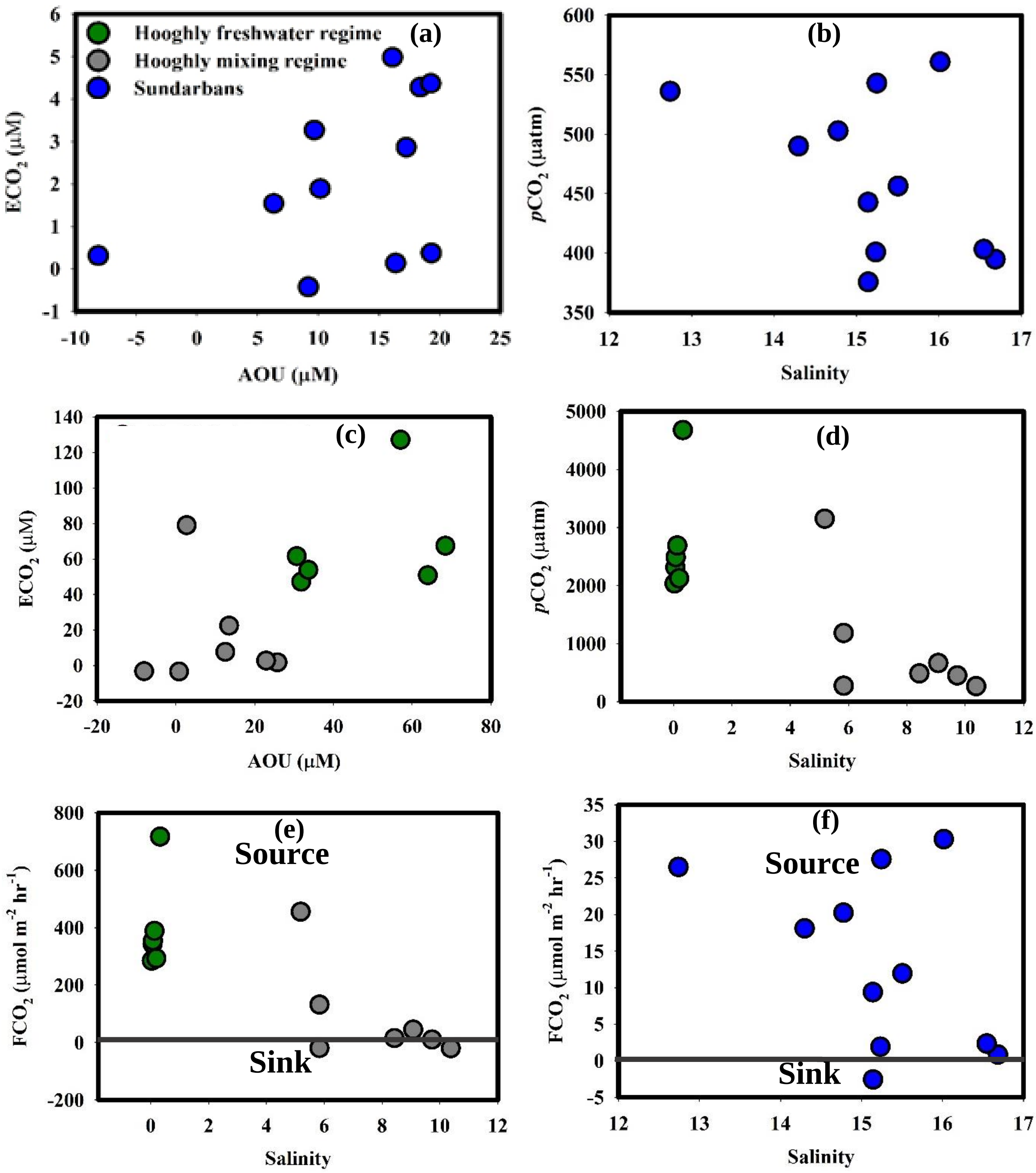

Hooghly freshwater regime
Hooghly mixing regime
Sundarbans
(a)
ECO$_2$ (µM)
AOU (µM)
(b)
pCO$_2$ (µatm)
Salinity
(c)
ECO$_2$ (µM)
AOU (µM)
(d)
pCO$_2$ (µatm)
Salinity
(e)
Source
Sink
FCO$_2$ (µmol m^{-2} hr^{-1})
Salinity
(f)
Source
Sink
FCO$_2$ (µmol m^{-2} hr^{-1})
Salinity

Fig. 6