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The post-monsoon 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 the post-monsoon 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 estuary (0.04–10.37). A mixing model suggested a combination of processes including freshwater intrusion, carbonate precipitation and carbonate dissolution to be a major factor controlling dissolved inorganic C (DIC) dynamics in the freshwater regime of the Hooghly, whereas phytoplankton productivity and CO_2 outgassing dominated in the mixing regime. In the Sundarbans, the removal of DIC (via CO_2 outgassing, phytoplankton uptake and export to the adjoining continental shelf region) dominated its addition through mineralization of mangrove-derived organic C. The concentration of dissolved organic C (DOC) in the Hooghly was ~ 40 % higher than in the Sundarbans, which was largely due to the 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 particulate organic C (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 with 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 the global carbon (C) cycle and the anthropogenic carbon dioxide (CO_2) budget (Bauer et al., 2013; Regnier et al., 2013; Le Quéré 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 (par-

ticulate organic C (POC): $0.13 \, \mathrm{Pg} \, \mathrm{C} \, \mathrm{yr}^{-1}$ and particulate inorganic C (PIC): $0.05 \, \mathrm{Pg} \, \mathrm{C} \, \mathrm{yr}^{-1}$) (Huang et al., 2012). Although estuaries are only $\sim 4\,\%$ 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 are not only active pathways for transport of C (Ittekkot and Laane, 1991) but also hotspots for biogeochemical modification of labile organic matter (OM) (Frankignoulle et al., 1998).

Mangroves covering $137\,760 \, \mathrm{km}^2$ along tropical and subtropical estuaries and coastlines (Giri et al., 2011) are among the most productive natural ecosystems in the world with net primary productivity of $218 \pm 72 \, \mathrm{Tg} \, \mathrm{C} \, \mathrm{yr}^{-1}$ (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 $\sim 10\,\%$ 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 a major C export pathway from mangrove forests, which was $\sim 70\,\%$ 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 (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 subsurface sediment layers and participates either in complex anaerobic processes (linked to production of biogenic trace gases like CH_4) or undergoes long-term sequestration (Jennerjahn 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 the inorganic and organic C biogeochemistry of a mangrove-dominated estuary. These processes largely depend upon pH, nutrient availability and 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 waste. 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). The lack of ample rate measurements of the 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 an uncertainty in the estimation of a coastal C budget on a global scale.

In India, research related to C biogeochemistry of estuarine ecosystems has been in focus since last two decades with an emphasis on estuaries located in southern India (e.g. Bouillon et al., 2003; Sarma et al., 2012, 2014; Bhavya et al., 2017, 2018). The estuaries located in the northern part of India have received limited attention, including the adjacently located Hooghly estuary and the estuaries of the Sundarbans, which are part of the Ganga–Brahmaputra river system (Fig. 1). Characteristically, the Hooghly and the estuaries of the 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 a supply of the industrial effluents and domestic sewage on a 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 the Sundarbans had been on the 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 the exception of one comprehensive study on nutrient budgets 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 $p\mathrm{CO_2}$ 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 the middle 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, the extrapolation of data

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

Parameters	Hooghly	Sundarbans
Nutrients (post-monsoon)	DIN: 14.72 ± 1.77 to $27.20 \pm 2.05\,\mu M$ DIP: 1.64 ± 0.23 to $2.11 \pm 0.46\,\mu M$ DSi: 77.75 ± 6.57 to $117.38 \pm 11.54\,\mu M$ Mukhopadhyay et al. (2006)	DIN: $11.70 \pm 7.65\,\mu M$ DIP: $1.01 \pm 0.52\,\mu M$ DSi: $75.9 \pm 36.9\,\mu M$ Biswas et al. (2004)
Chl a (post-monsoon)	2.35–$2.79\,\mathrm{mg\,m^{-3}}$ Mukhopadhyay et al. (2006)	$7.88 \pm 1.90\,\mathrm{mg\,m^{-3}}$ Dutta et al. (2015)
Population density	North 24 Parganas and Hooghly: $2500\,\mathrm{km^{-2}}$, Kolkata: $22\,000\,\mathrm{km^{-2}}$, Howrah: $3300\,\mathrm{km^{-2}}$, South 24 Parganas: $820\,\mathrm{km^{-2}}$	No major cities and towns
Freshwater discharge (post-monsoon)	3070–7301 million $\mathrm{m^3}$ Rudra et al. (2014)	No information available
Catchment area	$6 \times 10^4\,\mathrm{km^2}$ Sarkar et al. (2017)	No information available
Industrial and municipal waste-water discharge	1153.8 million $\mathrm{L\,d^{-1}}$ Ghosh, (1973), Khan (1995)	No information available
Dissolved metal flux	Increased from $230\,\%$ to $1770\,\%$ annually Samanta and Dalai (2018)	No information available

from these studies for the entire ecosystem may lead to overestimation and underestimation.

The primary objective of the present study was to understand differences in varied aspects of the C cycle (DIC, DOC, POC and CO_2) of the Hooghly and the estuaries of the Sundarbans during the post-monsoon season with relatively better spatial coverage compared to previous studies. The post-monsoon sampling was chosen because of relatively stable estuarine conditions for wider spatial coverage and peak mangrove leaf litter fall during this season (Ray et al., 2011), which may have an influence on estuarine C dynamics. Considering the different natures and quantities 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) the sources and fate of POC in these two contrasting systems, and (c) the partial pressure of CO_2 (pCO_2) and its controlling mechanisms along with exchange across the water–atmosphere interface at the Hooghly–Sundarbans during the post-monsoon period.

2 Materials and methods

2.1 Study area

The present study was carried out in the mangrove dominated estuaries of the Indian Sundarbans and anthropogenically dominated Hooghly estuary in northeastern India. The Sundarbans ($21°32'$ and $22°40'$ N: $88°05'$ and $89°$ 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 the $10\,200\,\mathrm{km^2}$ area of the Sundarbans, $41\,\%$ is in India and the rest is in Bangladesh. The Indian part of Sundarbans (or Sundarbans Biosphere Reserve) contains $4200\,\mathrm{km^2}$ of mangrove reserve forest and $1800\,\mathrm{km^2}$ 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*. A semidiurnal tide with a mean depth $\sim 6\,\mathrm{m}$ is a 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 the Sundarbans, tides are semidiurnal in nature in the Hooghly with variable depth along the channel ($\sim 21\,\mathrm{m}$ at Diamond Harbour (H6) to $\sim 8\,\mathrm{m}$
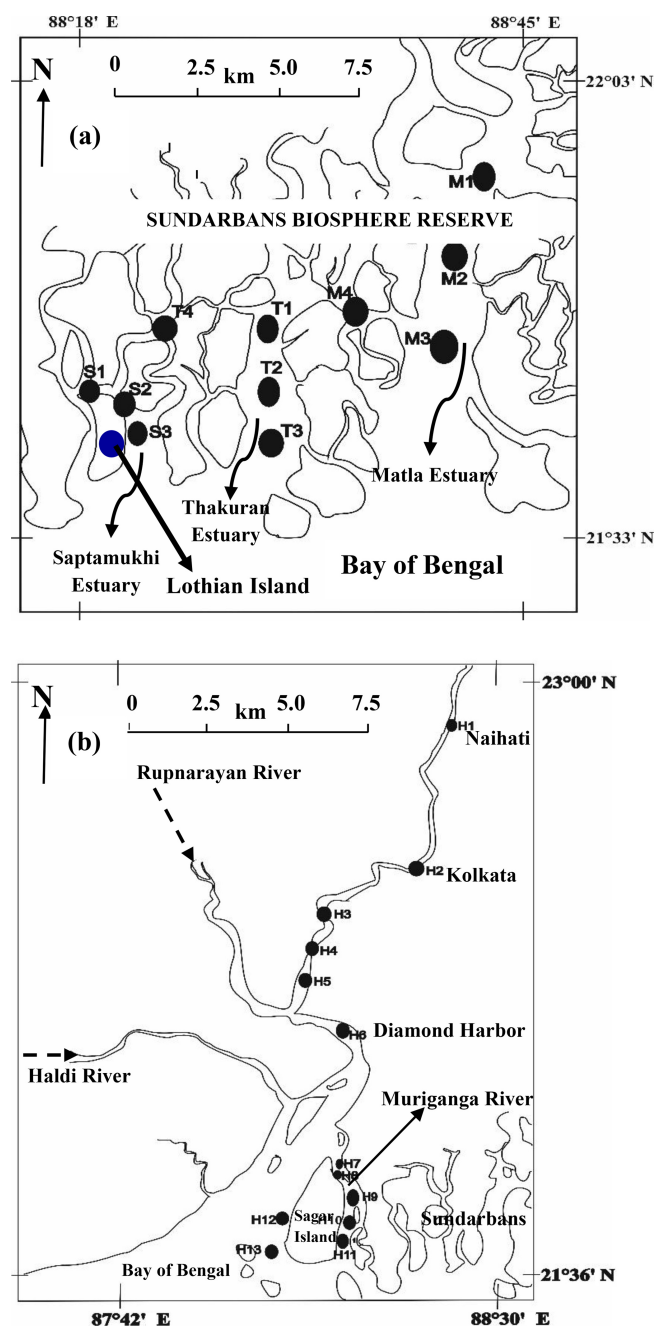
Figure 1. Sampling locations at the **(a)** estuaries of the Sundarbans and **(b)** Hooghly estuary.

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 a 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 a typical tropical climate with three distinct seasons: pre-monsoon (February–May),

monsoon (June–September) and post-monsoon (October–January) with ~ 80 % rainfall during monsoon.

Covering upper, middle and lower estuarine regions, the present study was carried out during low-tide conditions 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 and M4). The low-tide post-monsoon sampling was preferred as it was the 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 porewater) 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 described as the "Hooghly–Sundarbans system" and the estuaries of the Sundarbans will be called the "Sundarbans" unless discussed individually.

2.2 Sampling and experimental techniques

During the post-monsoon season (November 2016), estuarine surface water samples were collected in duplicate at different locations of the Hooghly–Sundarbans system using a 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 on board using a thermometer ($\pm 0.1\,^{\circ}$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: ± 0.1 mg L^{-1}) concentrations were measured on board 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 on board in a closed cell using 0.1 N HCl following the 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). Porewater was also collected from the lower littoral zone of the Lothian Island (one of the virgin islands of the Indian Sundarbans, Fig. 1a) by digging a hole (~ 30 cm below the water table). It was not possible to collect porewater samples from the middle and upper littoral zones

of the island due to logistic problems. After purging water at least twice in the bore, the sample was collected from the bottom of the bore through a 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 a 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 h) 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 °C during transportation to the laboratory. Additionally, micrometeorological parameters associated with the water–atmosphere CO_2 exchange flux computation continuously monitored at 10 m height over the estuary using a portable weather monitor (DAVIS – Vantage Pro2 Plus).

2.2.2 Laboratory measurements

The DIC concentrations were measured using Coulometer (model: UIC. Inc. CM – 5130) with an analytical uncertainty of ±0.8 %. The $\delta^{13}C_{DIC}$ were measured using GasBench II attached to a continuous flow mass spectrometer (Thermo Scientific MAT 253) with precision better than 0.10 ‰. The DOC was measured using a high-temperature catalytic oxidation analyzer (Shimadzu-TOC-L CPH), which was calibrated using a potassium hydrogen phthalate (KHP) solution containing 1, 2, 5, 10 and 20 mg L^{-1} of DOC (Ray et al., 2018). The analytical error for DOC measurement was < 2 %. For SPM measurements, filter paper containing SPM was dried in hot-air oven at 60 °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 decarbonated (by HCl fumes) and analysed using an 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} h^{-1}) across the water–atmosphere boundary of the

estuary were calculated as follows:

$$FCO_2 = k \times K_H^{CO_2} \times \left[pCO_{2\,(water)} - pCO_{2\,(atmosphere)} \right],$$

where $K_H^{CO_2} = CO_2$ 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 the Liss and Merlivat (1986) parametrization. For the same wind velocity, the parametrization of Liss and Merlivat (1986) provides the lowest 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 to be a conservative estimate. 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, last access: 10 May 2018) was corrected for water vapour partial pressure to calculate $pCO_{2\,(atmosphere)}$. The fraction, $K_H^{CO_2} \times [pCO_{2\,(water)} - pCO_{2\,(atmosphere)}]$ is the departure of free dissolved CO_2 from atmospheric equilibrium that may be termed "excess CO_2 (ECO_2)" (Zhai et al., 2005).

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

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

$$AOU = \left([O_2]_{Equilibrium} - [O_2]_{Measured}\right),$$

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), the conservative mixing model was applied to the Hooghly estuary to understand the addition or 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):

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

$$\delta^{13}C_{CM} = \frac{\left\{ \begin{array}{c} S_S \left[C_F \delta^{13}C_F - C_M \delta^{13}C_M \right] \\ + S_F C_M \delta^{13}C_M - S_M C_F \delta^{13}C_F \end{array} \right\}}{S_S (C_F - C_M) + S_F C_M - S_M C_F}.$$

Here, S denotes salinity, the suffixes CM, F, M and S denote conservative mixing, freshwater endmember, marine endmember and sample. F_F is freshwater fraction is $1 - (S_S / S_M)$

and F_M = marine water fraction is $(1 - F_F)$. $C_{Sample} > C_{CM}$ indicates C addition, whereas the 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 to be endmember values for freshwater, whereas respective values for marine end-members 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 the 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 the narrow salinity gradient (see later). However, assuming that apart from conservative mixing only mangrove-derived C ($\Delta C_{Mangrove}$) contributes to the estuarine C pool, an approach can be taken to quantify $\Delta C_{Mangrove}$. Two different mass balance equations 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 $-28.4\,\permil$ for the Sundarbans (Ray et al., 2015) and endmembers were taken to be the same as the Hooghly, as the estuaries of the Sundarbans are an offshoot of the 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 porewater exchange was calculated following Reay et al. (1995):

F_{DIC} = sediment porosity × mean linear velocity
  × mean pore water DIC conc.

Mean linear velocity = pore water specific discharge/
  sediment porosity.
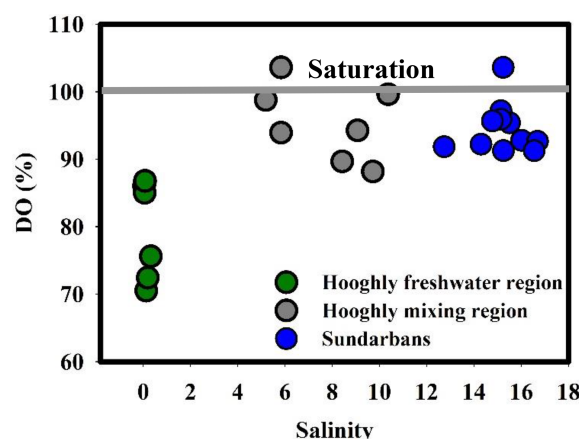
Figure 2. Percent saturation of DO–salinity relationship in the Hooghly–Sundarbans system.

3 Results

3.1 Environmental parameters

During the present study, the water temperature did not show any distinct spatial trend and varied from 28 to 29 °C and 30.5 to 33 °C for the Sundarbans (Table 2) and Hooghly (Table 3). Salinity of the estuaries of the Sundarbans varied over a narrow range (12.74 to 16.69; Table 2) with a 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) a freshwater regime (H1–H6) and (b) mixing regime (H7–H13; Fig. 1b). However, due to the narrow salinity range, no such classification was possible for the estuaries of the Sundarbans. The estuaries of the Sundarbans were relatively well-oxygenated (DO = 91 % to 104 %) compared to the Hooghly estuary (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 the 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

Table 2. Physicochemical parameters, inorganic and organic C-related parameters and CO_2 exchange flux across the water–atmosphere interface at the estuaries of the Sundarbans. Here, W_T is water temperature, DO is dissolved oxygen.

Station	W_T (°C)	Salinity	DO (mg L^{-1})	pH	DIC (µM)	$\delta^{13}C_{DIC}$ (‰)	DOC (µM)	POC (µM)	$\delta^{13}C_{POC}$ (‰)	pCO_2 (µatm)	FCO_2 (µmol m^{-2} h^{-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 the water–atmosphere interface at the Hooghly estuary. Here, W_T is water temperature, DO is dissolved oxygen.

Station	W_T (°C)	Salinity	DO (mg L^{-1})	pH	DIC (µM)	$\delta^{13}C_{DIC}$ (‰)	DOC (µM)	POC (µM)	$\delta^{13}C_{POC}$ (‰)	pCO_2 (µatm)	FCO_2 (µmol m^{-2} h^{-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

lower estuarine regions, with a 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 11 756 µM, $\delta^{13}C_{DIC} = −12.66$‰ to $−6.67$‰; Sundarbans: DIC = 7524 to 13 599 µM, $\delta^{13}C_{DIC} = −10.56$‰ to $−6.69$‰; Table 4) and porewater samples (Sundarbans: DIC = 13 425 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, $\sim 40\%$ higher DOC was noticed in the Hooghly (235 to 662 µM; Table 3), reaching a 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: $−23.36 \pm 0.32$‰), whereas in the Hooghly it varied from $−26.28$‰ to $−23.47$‰ (mean: $−24.87 \pm 0.89$‰).

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

Table 4. The DIC concentrations and $\delta^{13}C_{DIC}$ of groundwater (GW) and porewater (PW) samples collected around the Hooghly–Sundarbans system.

Ecosystems	Station	DIC (µM)	$\delta^{13}C_{DIC}$ (‰)
Hooghly	H3GW	11 756	−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	13 425	−18.05
	Kalash GW	13 599	−6.69
	Virat Bazar GW	8300	−10.56

was estimated in the Hooghly estuary (267 to 4678 µatm; Table 3), reaching its peak in the freshwater regime. Except for 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} h^{-1}; mean: 231 µmol m^{-2} h^{-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} h^{-1}; Table 2). Spatially, in the Hooghly, higher FCO_2 was noticed in the freshwater regime (285.2 to 717.5 µmol m^{-2} h^{-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 the 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 the potential influence of marine and freshwater mixing on DIC and $\delta^{13}C_{DIC}$ in the estuary (Fig. 3a, b), rationalizing the application of a two-endmember mixing models. A two-endmember mixing model to decipher processes influencing

DIC chemistry has been applied earlier in the Hooghly estuary (Samanta et al., 2015).

Based on the methodology discussed earlier, calculated ΔC for DIC ($\Delta DIC \sim -0.27$ to 0.17) predicted a 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 the 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. A deviation plot (ΔDIC vs. $\Delta\delta^{13}C_{DIC}$; Fig. 3c) for samples of the Hooghly showed the following patterns: (a) a decrease in ΔDIC with increasing $\Delta\delta^{13}C_{DIC}$ ($n = 5$), indicating phytoplankton productivity and/or outgassing of CO_2 across the water–atmosphere interface, (b) a 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 the 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 conditions during the post-monsoon season in the Hooghly (Mukhopadhyay et al., 2002., 2006). However, based on the present data, particularly due to a 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 rivers, two mangrove-dominated rivers of peninsular Thailand flowing towards the 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 rivers: sharp salinity gradient (∼ 0 to 35); Miyajima et al., 2009). Like Hooghly, the $\delta^{13}C_{DIC}$–salinity relationship was statistically significant ($r^2 = 0.55$, $p = 0.009$) for the Sundarbans, but the DIC–salinity relationship remained insignificant ($p = 0.18$) (Fig. 3d, e).

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
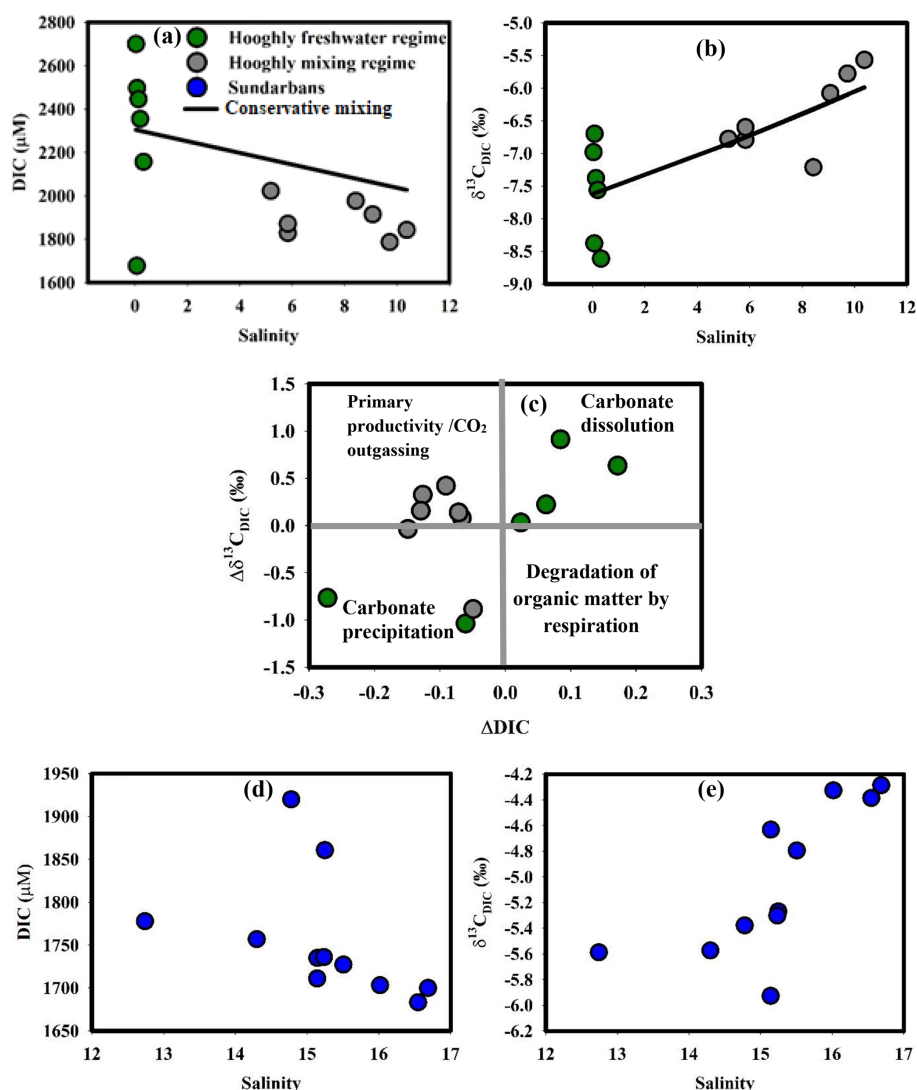
Figure 3. (a) DIC–salinity in the Hooghly, **(b)** $\delta^{13}C_{DIC}$–salinity in the Hooghly, **(c)** ΔDIC–$\Delta\delta^{13}C_{DIC}$ in the Hooghly, **(d)** DIC–salinity in the Sundarbans and **(e)** $\delta^{13}C_{DIC}$–salinity in the Sundarbans.

(ΔDIC$_{Mangrove}$) estimated based on DIC (ΔDIC$_{M1}$) and $\delta^{13}C_{DIC}$ (ΔDIC$_{M2}$) should be equal. The negative and un-equal values of ΔDIC$_{M2}$ (-41 to $62\,\mu$M) and ΔDIC$_{M1}$ (-186 to $11\,\mu$M) indicate a large DIC outflux over influx through mineralization of mangrove-derived OC in this trop-ical 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 lo-cations covered; see Sect. 4.4). Also, a recent study by Ray et al. (2018) estimated DIC export ($\sim 3.69\,\text{Tg C yr}^{-1}$) from the estuaries of the Sundarbans as the dominant form of C export. Although data for primary productivity is not avail-able for the study period, earlier studies have reported post-

monsoon as the peak season for phytoplankton productivity (Biswas et al., 2007; Dutta et al., 2015). Given the evidence for the 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 un-derstand the balance between influx and outflux of DIC in the Sundarbans.

Other than biogeochemical processes, factors such as groundwater and porewater 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, espe-cially within carbonate aquifer region (Cai et al., 2003). Al-though all the parameters of groundwater inorganic C sys-tem (like pH, TAlk and pCO$_2$) were not measured dur-ing the present study, groundwater DIC was ~ 5.57 and

~ 3.61 times higher compared to mean surface water DIC in the Sundarbans and Hooghly. The markedly higher DIC in groundwater, as well as the similarity in its isotopic composition with estuarine DIC, may stand as a signal for the influence of groundwater on estuarine DIC, with a possibly greater influence in 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 a low-salinity regime (salinity < 10, same as our salinity range) based on Ca measurement, which was not observed based on the Ra isotope measurement in an earlier study (Somayajulu et al., 2002). Porewater DIC in the Sundarbans was ~ 7.63 times higher than the estuarine water, indicating the possibility of DIC input from the adjoining mangrove system to the estuary through porewater exchange depending upon changes in hypsometric gradient during tidal fluctuation (i.e. tidal pumping). By using porewater-specific discharge and porosity at $0.008 \, \mathrm{cm \, min^{-1}}$ and 0.58 (Dutta et al., 2013, 2015), respectively, during the post-monsoon season and extrapolating the flux value on a daily basis (i.e. for 12 h as tides are semidiurnal in nature), mean F_{DIC} during the post-monsoon season was calculated as $\sim 770.4 \, \mathrm{mmol \, m^{-2} \, d^{-1}}$. However, the significant impact of porewater on DIC may be limited only in mangrove creek water (samples not collected) as evident from the 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 porewater-mediated DIC additions is needed to thoroughly understand their importance in controlling the 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 the degree of biogeochemical and hydrological processes. A relatively higher freshwater contribution in the Hooghly compared to the Sundarbans (as evident from salinity), as well as significant negative relationship between DIC and salinity, proved the 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.

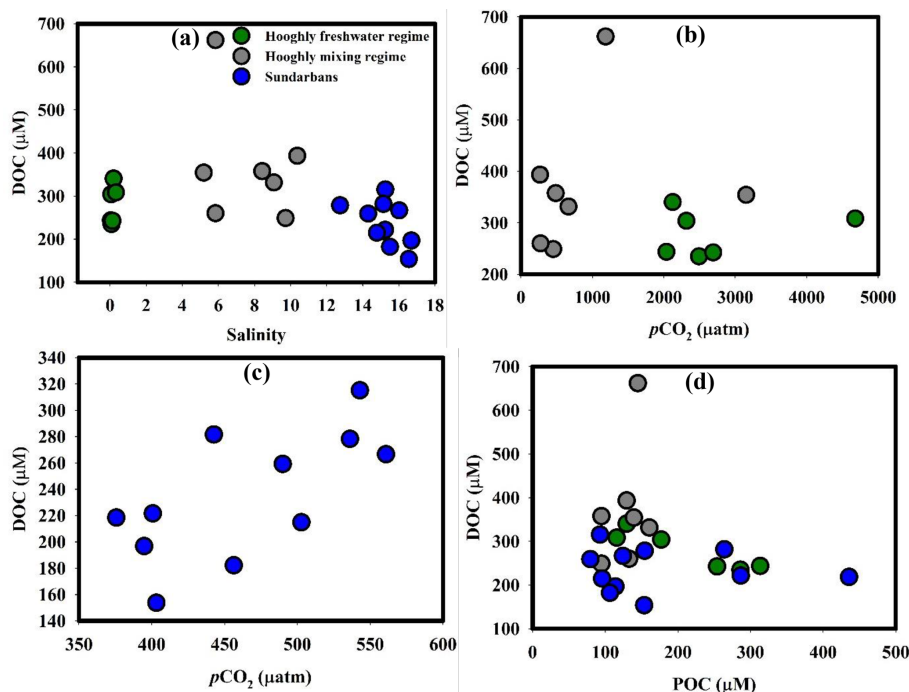## 4.2 DOC in the Hooghly–Sundarbans

In the Hooghly, DOC concentrations observed during this study was higher than the range (226.9 ± 26.2 to $324 \pm 27 \, \mu M$) reported by Ray et al. (2018), whereas observed DOC in the Sundarbans was comparable with their estimates ($262.5 \pm 48.2 \, \mu M$). The marine water and freshwater mixing did not appear to exert major control over DOC in the Hooghly–

Sundarbans system as evident from the 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 subtropical estuarine system is principally controlled by processes other than the 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 ($\Delta DOC = -0.16$ to 0.11), whereas only net addition was evident throughout the mixing regime ($\Delta DOC = 0.08$ to 1.74). In the Sundarbans, except the lower Thakuran (St. T3, $\Delta DOC_{M1} = -20 \, \mu M$), net addition of mangrove-derived DOC was estimated throughout ($\Delta DOC_{M1} = 2$ to $134 \, \mu M$).

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 the $\delta^{13}C_{DIC}$ and POC relationship ($r^2 = 0.68$, $p = 0.05$), further evaluation of its impact on DOC was not possible due to the lack of direct measurement. Contradictory results exist regarding the influence of phytoplankton productivity on DOC. Some studies did not find a direct link between DOC and primary productivity (Boto and Wellington, 1988), whereas a significant contribution of phytoplankton production to building a DOC pool ($\sim 8\%$ to 40 %) has been reported by others (Dittmar and Lara, 2001; Kristensen and Suraswadi, 2002).

In a nutrient-rich estuary like Hooghly, the lack of a significant relationship between DOC and $p CO_2$ (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, a significant positive relationship between these two in the Sundarbans ($r^2 = 0.45$, $p = 0.02$, Fig. 4c) indicated an increase in aerobic bacterial activity with increasing DOC. In mangrove ecosystems, leaching of mangrove leaf litter as DOC is as fast as $\sim 30\%$ of mangrove leaf litter leaching as DOC is reported within the initial 9 days of degradation (Camilleri and Ribi, 1986). In the Sundarbans, mangrove leaf litter fall peaks during the post-monsoon season (Ray et al., 2011) and its subsequent significant leaching as DOC was evident during the

Figure 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.

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 with Bouillon et al. (2003) for the Godavari estuary, southern India.

Despite high-water residence time in the Hooghly ($\sim$ 40 days during the post-monsoon season; Samanta et al., 2015) and in mangrove ecosystems like the Sundarbans (Alongi et al., 2005; Singh et al., 2016), DOC photooxidation may not be so potent due to unstable estuarine conditions 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 favour 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 freshwater (river) and seawater and the coagulation mostly completes within the 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 a poten-

tial contribution from external sources that may include industrial effluents and municipal waste-water discharge (i.e. surface runoff) in the freshwater regime of the Hooghly (Table 1). However, there are no direct DOC influx data available to corroborate the same. Relatively higher amounts of 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 a lack of isotopic data. Considering significantly high DOC levels in waste water effluent (Katsoyiannis and Samara, 2006, 2007), along with fast degradation of biodegradable DOC ($\sim$ 80 % within 24 h; Seidl et al., 1998) and residence time of Hooghly water (mentioned earlier), Samanta et al. (2015) suggested the 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 $\sim$ 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 addition is warranted.

Overall, on average, the concentration of DOC in the Hooghly was $\sim 40\%$ higher than in the Sundarbans, which appeared to be due to the 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 the 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 $129.7 \pm 6.7\,\mu M$, Sundarbans: $45.4 \pm 7.5\,\mu M$) reported by Ray et al. (2018) for the Hooghly–Sundarbans system. However, it was within the range (51 to $750\,\mu M$; 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, b), 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, the contribution of POC via surface runoff is also a possibility in this regime due to the presence of several industries and large urban population (St. H2: Megacity Kolkata) that discharge industrial effluents and municipal waste water to the estuary on a regular basis (Table 1). A signal for surface-runoff-mediated POC addition was evident in the freshwater regime where $\sim 61\%$ and $\sim 43\%$ 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. A 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 a high SPM load (Ittekkot and Laane, 1991) as observed in the mangrove-dominated Godavari estuary in southern India (Bouillon et al., 2003).

In general, wide ranges for $\delta^{13}C$ (rivers $\sim -28\%_o$ to $-25\%_o$; marine plankton $\sim -22\%_o$ to $-18\%_o$; C_3 plant $\sim -32\%_o$ to $-24\%_o$; C_4 plants $\sim -13\%_o$ to $-10\%_o$; freshwater algae and their detritus $\sim -30\%_o$ to $-40\%_o$) have been reported in the 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 an influx of POC via freshwater runoff as well as terrestrial C_3 plants. Additionally, the es-

tuary was also anthropogenically stressed during the post-monsoon season with measured $\delta^{13}C_{POC}$ within the range reported for sewage ($\delta^{13}C_{POC} \sim -28\%_o$ to $-14\%_o$, Andrews et al., 1998; $\delta^{13}C_{DOC} \sim -26\%_o$, 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 the Sundarbans, isotopic signatures of POC showed similarity with terrestrial C_3 plants. Interestingly, despite being a mangrove-dominated estuary (salinity: 12.74 to 16.55), no clear signature of either freshwater or mangrove-borne ($\delta^{13}C$: mangrove leaf $\sim -28.4\%_o$, soil $\sim -24.3\%_o$, Ray et al., 2015, 2018) POC was evident from $\delta^{13}C_{POC}$ values, suggesting the possibility of significant POC modification within the system. Modification of POC within the estuaries of Indian subcontinent has been reported earlier (Sarma et al., 2014). Inter-estuary comparison revealed relatively lower average $\delta^{13}C_{POC}$ at the Hooghly (mean $\delta^{13}C_{POC}$: $-24.87 \pm 0.89\%_o$) compared to the Sundarbans (mean $\delta^{13}C_{POC}$: $-23.36 \pm 0.32\%_o$), which appeared to be due to differences in degree of freshwater contribution, anthropogenic inputs (high in Hooghly vs. little/no in Sundarbans), the 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 ($\Delta POC = -0.45$ to 0.48), whereas removal ($n = 6$) dominated over addition ($n = 1$) in the mixing regime ($\Delta POC = -0.39$ 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 the case of an oxygenated estuary.

The plot between $\Delta\delta^{13}C$ for POC ($\Delta\delta^{13}C_{POC}$) and ΔPOC (Fig. 5d) indicated that different processes are active in different regimes of the Hooghly estuary. The decrease in ΔPOC with an 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 the estuarine CO_2 pool as evident from the POC–pCO_2 relationship (freshwater regime: $p = 0.29$, mixing regime: $p = 0.50$; Fig. 5e). A decrease in both ΔPOC and $\Delta\delta^{13}C_{POC}$ ($n = 2$ for mixing regime and $n = 2$ for freshwater regime) supported the settling of POC to subtidal sediment. Despite high-water residence time, this process may not be effective in the Hooghly due to unstable estuarine conditions (described earlier). An increase in ΔPOC with a decrease in $\Delta\delta^{13}C_{POC}$ ($n = 2$ for the freshwater regime) indicated POC inputs via surface and freshwater
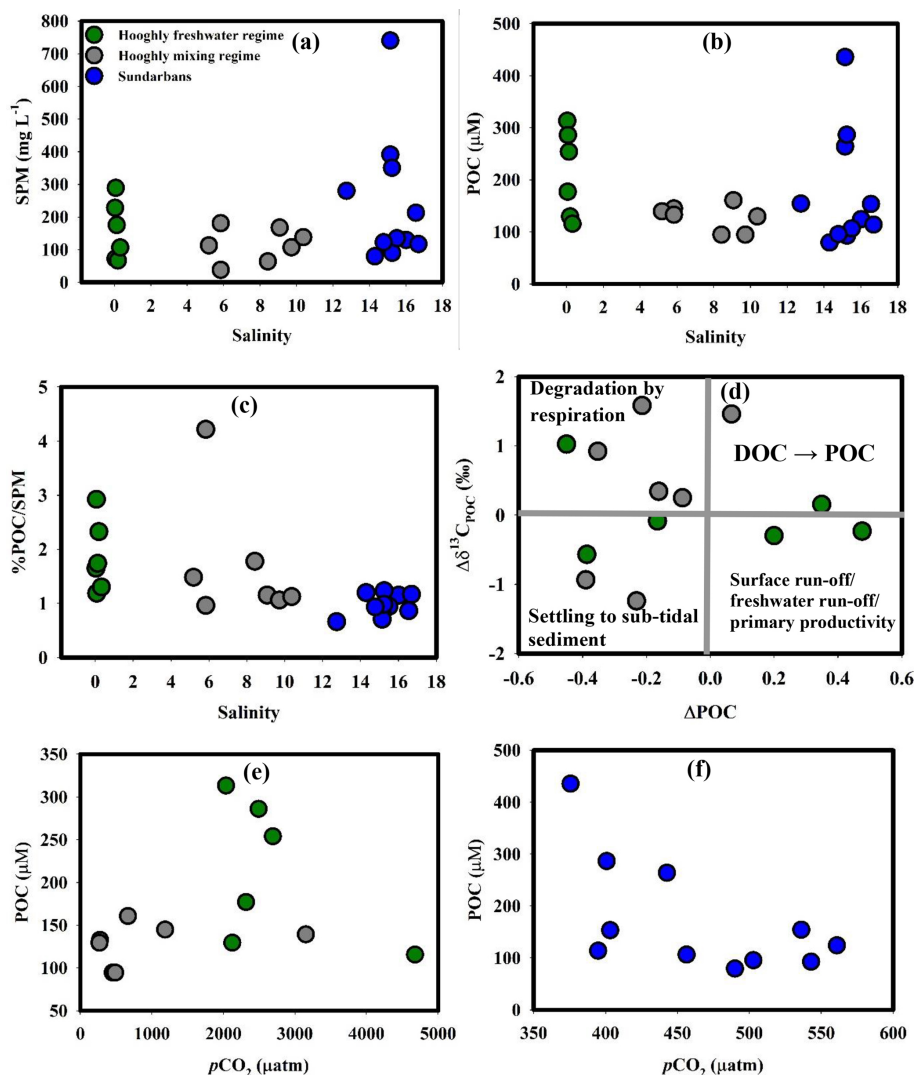
Figure 5. (a) SPM–salinity in the Hooghly–Sundarbans system, **(b)** POC–salinity in the Hooghly–Sundarbans system, **(c)** % POC / SPM–salinity in the Hooghly–Sundarbans system, **(d)** ΔPOC–$\Delta\delta^{13}$C$_{POC}$ in the Hooghly, **(e)** POC–pCO$_2$ in the Hooghly and **(f)** POC–pCO$_2$ in the Sundarbans.

runoff as well as phytoplankton productivity. An 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 $-28\,\mu$M) compared to ΔPOC$_{M1}$ (-35 to $327\,\mu$M) suggested DIC-like behaviour, i.e. simultaneous removal or modification along with the addition of mangrove-derived POC. No evidence for in situ POC–DOC exchange was found based on the POC–DOC relationship; however, the signal for degradation of POC by respiration was evident in the Sundarbans from the POC–pCO$_2$ relationship ($r^2 = 0.37$, $p = 0.05$, Fig. 5f). Similarly to the Hooghly, despite high-water residence time in mangroves (Alongi et al., 2005; Singh et al., 2016), unstable estuarine conditions may not favour efficient

settlement of POC at subtidal 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 and ~ 0.58 Tg 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$_2$ values 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 percent saturation of DO
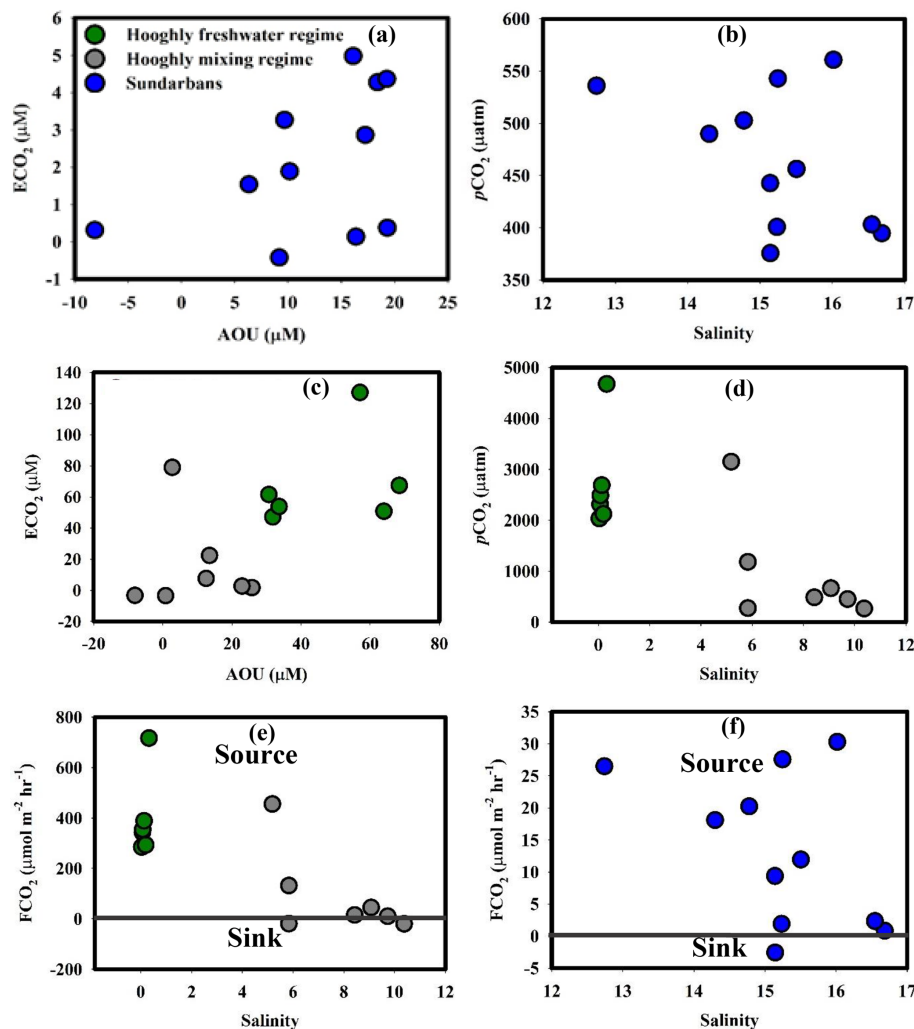
Figure 6. (a) ECO_2–AOU in the Sundarbans, **(b)** pCO_2–salinity in the Sundarbans, **(c)** ECO_2–AOU in the Hooghly, **(d)** pCO_2–salinity in the Hooghly, **(e)** FCO_2–salinity in the Hooghly and **(f)** FCO_2–salinity in the Sundarbans.

($r^2 = 0.76$, $p = 0.005$; figure not given) suggested the 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 ($ECO_2 = 0.057$ AOU $+ 1.22$, $r^2 = 0.76$, $p = 0.005$, $n = 8$; 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 subtropical estuary, Pearl River estuary, China (Zhai et al., 2005). However, a relatively lower slope for ECO_2–AOU relationship (0.057) compared to the slope for Redfield respiration in a HCO_3^--rich environment $((CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 18HCO_3^- \rightarrow$ $124CO_2 + 140H_2O + 16NO_3^- + HPO_4^{2-}$; 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 the formation of low molecular weight OM instead of the final product (CO_2) during aerobic OM respiration (Zhai et al., 2005). Moreover, the pCO_2–salinity relationship ($p = 0.18$, Fig. 6b) confirmed no significant effect of freshwater and marine water contribution on variability of pCO_2 in the Sundarbans. Other potential sources of CO_2 to the mangrove-dominated Sundarbans could be groundwater (or pore water) exchange across the intertidal mangrove sediment–water interface. Although based on our own data set, it is not possible to confirm the same. However, relatively higher pCO_2 levels during low tide compared to high tide at the 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, the ECO_2–AOU relationship did not confirm the 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 runoff 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 the freshwater regime of the Hooghly (Tables 2 and 3). A lack of negative correlation between pCO_2 and salinity in freshwater regime (Fig. 6d) of the Hooghly suggested a limited contribution of CO_2 due to freshwater input. Therefore, CO_2 supply via surface runoff may be the 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 post-monsoon (Fig. 6e, f). Specifically, from regional climate and environmental change perspectives, the anthropogenically influenced Hooghly estuary was a relatively greater source of CO_2 to the regional atmosphere compared to the mangrove-dominated Sundarbans ($[FCO_2]_{\text{Hooghly}}$: $[FCO_2]_{\text{Sundarbans}} = 17$). However, despite being a CO_2 source, FCO_2 measured for the estuaries of the Sundarbans were considerably lower compared to global mean FCO_2 reported for the mangrove-dominated estuaries (~ 43 to $59 \, \text{mmol C m}^{-2} \, \text{d}^{-1}$; 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: $46 \, \text{mmol m}^{-2} \, \text{d}^{-1}$, Guo et al., 2009; Yangtze River estuary: $41 \, \text{mmol m}^{-2} \, \text{d}^{-1}$, 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 the water–atmosphere interface. Quantitatively, the difference in k values for the Hoogly and Sundarbans were not large ($k_{\text{Sundarbans}} - k_{\text{Hooghly}} \sim 0.031 \, \text{cm h}^{-1}$). Therefore, large difference in FCO_2 between these two estuarine systems may be due to a 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 the post-monsoon season. Considering the different natures and quantities 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 regions) and the 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 contributing to the POC pool in the Hooghly, whereas a 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 a source of CO_2 to the regional atmosphere with ~ 17 times higher emission from the Hooghly compared to the Sundarbans, suggesting a significant role played by an anthropogenically stressed estuarine system from regional climate change perspectives.

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

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