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Reviews and Syntheses: Carbon biogeochemistry of Indian estuaries

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Abstract

The goal of this review is to provide a comprehensive overview of the magnitude and drivers of carbon cycling dynamics in the major estuaries of India. Data from a total of 32 estuaries along the Bay of Bengal (BB) and the Arabian Sea (AS) were compiled from the literature and re-analysed based on changes in season (wet vs. dry) and marine end-members (e.g., BB vs. AS). The estuaries are generally undersaturated in dissolved oxygen relative to the atmosphere and strongly influenced by local and regional precipitation patterns. Speciation of the dissolved inorganic carbon (DIC) pool is dominated by bicarbonate and primarily variability in DIC is controlled by a combination of carbonate weathering, the degree of precipitation, the length of the estuaries, in situ respiration, and mixing. Carbonate dissolution had the largest influence on DIC during the wet season, while respiration was the primary control of DIC variability in the estuaries connected with BB during the dry season. Interestingly, the influence of anaerobic metabolism on DIC is observed in the oxygenated mangrove dominated estuaries, which we hypothesize is driven by porewater exchange in intertidal sediments. Dissolved organic carbon (DOC) generally behaves non-conservatively in the studied estuaries. The DOC-particulate organic carbon (POC) inter-conversion and DOC mineralization are evident in the BB during the dry season and AS estuaries, respectively. The wet season $\delta^{13}C_{POC}$ shows dominance of freshwater algae, C_3 plant material, as well as marine organic matter in POC. However, anthropogenic inputs are evident in some estuaries in eastern India during the dry season. POC respiration was identified in the AS; however, a link between POC and CH_4 is identified throughout both the regions. pCO$_2$ is controlled principally by respiration with freshwater discharge only playing a marginal important role in the BB. The AS estuaries act as a CO_2 source to the atmosphere; however, the BB estuaries vary between a source and sink. POC together with methanotrophy and dam abundance appear to control CH_4 concentrations, and all of the studied estuaries act as a CH_4 source to the atmosphere. Additionally, anthropogenic inputs and groundwater exchange also show potential influences in some cases. The Indian estuaries contribute 2.62% and 1.09% to the global riverine DIC and DOC exports to the ocean, respectively. The total

CO_2 and CH_4 fluxes from Indian estuaries are estimated as ~9718 Gg yr^{-1} and 3.27 Gg yr^{-1}, which contributes ~0.67% and ~0.12%, respectively, to global estimates of estuarine greenhouse gas emissions. While a qualitative idea on the major factors controlling the carbon biogeochemistry in India is presented through this work, a more thorough investigation including rate quantification of the above-mentioned mechanisms is essential for precise accounting of the C budget of Indian estuaries.

Keywords

Carbon cycling, trace gases, estuary, mangroves, India

Introduction

Estuaries, where inland waters mix with the coastal ocean, serve as important centres of C cycling at the land-ocean interface (e.g., Bianchi et al 2018). These dynamic ecosystems with abundant biodiversity and biological activity are emerging as a net source of carbon dioxide (CO_2) and methane (CH_4) to the atmosphere as most of the world's large rivers and estuaries are being reported to be oversaturated with respect to CO_2 and CH_4 (Bouillon et al., 2003). A fraction of CO_2 removed from the atmosphere by terrestrial systems during photosynthesis and weathering reactions is exported into rivers and estuaries as inorganic and organic carbon; a significant portion of this exported C is ultimately recycled back into the atmosphere (Ward et al., 2017). Although estuaries only cover ~4% of the continental shelf regions, globally, the amount of CO_2 outgassed from estuaries is similar to CO_2 uptake in continental shelf regions of the world, albeit with large uncertainty (Borges et al., 2003; Cai et al., 2003; Cai and Wang, 1998). This suggests that estuaries are not only active pathways for C transport (Bianchi and Bauer, 2011; Bauer and Bianchi, 2011; Dutta et al., 2019a) but potentially a niche for labile OM modification by biogeochemical processes (Frankignoulle et al., 1998; Bianchi 2011). In addition, surface run off, anthropogenic activities (including both municipal as well as industrial) and groundwater inputs also contribute to the estuarine C pool. Thereafter, based upon oxygen levels and residence time in the estuary, among other factors, C undergoes complex biogeochemical transformations before transiting to the continental shelf region and/or atmosphere.

Rivers are the major source of organic matter (OM) to the coastal environment as they transport OM derived from vascular plants and soils from the terrestrial environment to the ocean (Onstad et al., 2000; Li et al., 2017; Raymond et al., 2001). Lateral export from coastal wetlands and subterranean groundwater discharge also deliver OM to estuaries, but these fluxes remain poorly constrained (Moore and Joy, 2021; Santos et al., 2021). The terrestrial OM derived from continental land masses is one of the major energy sources for aquatic and marine organisms (Sedell et al., 1989; Wang et al., 2014; Krishna et al., 2015). Therefore, riverine transport of OM is not only directly link with the global C cycle but also plays a

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pivotal role in the food web dynamics of freshwater and coastal ecosystems (Caffrey, 2004). Contributing ~66% of global river water discharge, tropical rivers deliver ~0.53 Pg C to estuaries annually (Huang et al., 2012) of which dissolved organic C (DOC) and particulate organic C (POC) contribute ~210 and 170 Tg C yr^{-1}, respectively (Ludwig et al., 1996). Along with rivers, tidal vegetated wetlands (mangroves, salt marshes, and seagrass), also play a significant role in the coastal ocean (<200 m water depth, covering ~7% of the ocean surface) C budget (Bauer et al., 2013; Rosentreter et al., 2018). Very similar to the estuaries, the tidal vegetated wetlands act as a lateral C filter as well as a hotspot for biogeochemical C transformation (Koné and Borges, 2008, Nellemann et al., 2009; Mcleod et al., 2011; Breithaupt et al., 2012, Regnier et al., 2013; Rosentreter et al., 2018; Dutta et al., 2019a). Despite having immense biogeochemical significance, the tidal vegetated wetlands are disappearing at an alarming rate on annual scale (mangroves: ~0.7 – 3%; seagrass: ~7%, saltmarsh: ~1 – 2%; Mcleod et al., 2011). Therefore, comprehensive investigation of them is needed to understand implication of ecosystem loss on coastal C biogeochemistry as well as more precise accounting of global C budgets (Alongi, 2002; Mcleod et al., 2011; Bauer et al., 2013).

While substantial insight has been gained on estuarine OC cycling and CO_2 exchange, the magnitude of CH_4 emissions or uptake by estuaries remains poorly constrained. Aquatic ecosystems account for nearly half of global emissions of CH_4 from natural and anthropogenic sources; estuaries and coastal vegetated ecosystems only account for a small amount of these aquatic emissions (Al-Haj and Fulweiler, 2020; Saunois et al., 2020). However, biogenic CH_4 emissions from aquatic systems, including estuaries, are likely to increase with increasing coastal urbanization and eutrophication (Rosentreter et al., 2021). Further, the abundance of thermogenic sources of CH_4 in tectonically active estuarine seafloors remain poorly documented and potentially large positive feedback for climate change (Johnson et al., 2022).The coast of India is home to numerous and diverse estuarine systems facing varying degrees of anthropogenic pressure; to date, studies of Indian estuaries have largely focused on either single estuaries with wide spatial coverage (Mukhopadhyay et al., 2006; Samanta et al., 2015; Dutta et al., 2019a, 2021; Gupta et al., 2008; Pattanaik et al., 2017; Bhavya et al., 2017; Bouillon et al., 2003; Sarma et al., 2011), or a large number of estuaries with limited sampling locations (Sarma et al., 2012, 2014; Krishna et al., 2015, 2019; Rao et al., 2016). Moreover, many of these estuaries have extensive coastal wetlands, particularly mangroves, which are densely distributed in estuaries of the Sundarbans (Saptamukhi, Thakuran, and Matla) and more sparsely scattered along the banks of the Haldia, Mahanadi, Godavari, Krishna, Ponnayaar, Mandovi and Zuari Rivers (Dutta et al., 2015; Rao et al., 2016).

In general, the C biogeochemistry of Indian estuaries bordered by extensive mangrove systems, has received more attention than estuaries less influenced by mangroves (Biswas et al., 2004, 2007; Mukhopadhyay et al., 2002; Dutta et al., 2013, 2015, 2017, 2019a, 2019b, 2021; Ray et al., 2011, 2013, 2015, 2018; Ganguly et al., 2011; Krithika et al., 2008; Borges et al., 2003; Akhand et al., 2016, 2021). Some studies have focused on key drivers of OM cycling (Sarma et al., 2012, 2014; Dutta et al., 2019a, 2021; Rao et al., 2016; Ray et al., 2011, 2013; Biswas et al., 2004, 2007; Mukhopadhyay et al., 2002), and others more on quantitative assessments of C budgets (Dutta et al., 2013, 2015, 2017) and export fluxes (Ray et al., 2018; Krishna et al., 2015, 2019). Nevertheless, there remain gaps in our knowledge on how changes in seasons (wet vs. dry) and marginal seas (Bay of Bengal BB vs. Arabian Sea AS) fit into the larger view of estuarine C processing in the dynamic coastal region. Additionally, to our knowledge, there is no comprehensive review on C and trace gas (CO_2 & CH_4) cycling of Indian major estuaries. In this review, the key objectives of this work are to: examine differences in the major drivers of dissolved and particulate C biogeochemistry of the BB and AS estuaries; understand basic differences in major controlling factors for the CO_2 and CH_4 cycling of the BB and AS estuaries; and establish the importance of major Indian estuaries in regional and global C budgets.

Study area

The Indian sub-continent is located at the centre of the monsoon domain and comprises three distinct zones—Peninsula, Indo-Gangetic alluvium and Extra-Peninsula—

each with distinct climatic and geo-environmental settings. The monsoon system is significantly influenced by the orographic systems, which creates spatial disparity in the monsoon rainfall across India. Global change in the monsoon system and hydrological regime (Mathew et al., 2021) are inherently linked with C biogeochemistry of the Indian estuaries.

The Indian Ocean includes the Arabian Sea, Laccadive Sea, Somali Sea, Andaman Sea, and the Bay of Bengal, which collectively cover ~19.8% of the water on the Earth's surface. The Indian Ocean is unique in terms of its geographic position as it is surrounded by Asia to the north, Africa to the west, and Australia to the east. The Indian sub-continent diverges the northern Indian Ocean into the Bay of Bengal (NE Indian Ocean) and Arabian Sea (NW Indian Ocean) with ~5 times higher freshwater discharge to the former (1.63×10^{12} $m^3 yr^{-1}$) (Subramanian, 1993; Gauns et al., 2005). The large freshwater influx to the BB leads to the development of a strong vertical salinity stratification that prevents vertical mixing between nutrient rich subsurface water with the surface. Additionally, higher suspended sediment loads limit the euphotic depth (Subramanian, 1993; Prasanna Kumar et al., 2002; Madhupratap et al., 2003) thereby limiting the phytoplankton growth. The coupled interaction limits productivity in the BB (Varkey et al., 1996; Prasanna Kumar et al., 2002). In contrast, the strong upwelling together with convective mixing present in AS makes it as one of the most productive regions in the world (Madhupratap et al., 1996; Muraleedharan and Prasanna Kumar, 1996; Bhattathiri et al., 1996; Barber et al., 2001).

Freshwater discharge from Indian rivers is principally governed by the monsoon-induced precipitation during the southwest (SW) monsoon (June – September, > 80% of its annual rainfall; Soman and Kumar, 1990) with occasional rainfall during the northeast (NE) monsoon (December - March) that is mostly stored in dam reservoirs for domestic, industrial and irrigation uses. Due to minimal discharge during the non-monsoon period, the discharge during the SW monsoon is considered to be roughly equivalent to the total annual discharge for Indian rivers. The magnitude of discharge from these rivers depends on spatial variations in rainfall over the catchment during SW monsoon with comparatively higher precipitation along the SW (3000 mm) followed by the NE (1000 - 2500 mm), SE (300 - 500 mm) and

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NW (200 - 500 mm) coasts of India (Soman and Kumar, 1990). Variability in discharge changes the dominant source of organic matter inputs in Indian rivers (allochthonous or autochthonous) and the contribution of these sources varies between estuaries depending on river basin size, tidal amplitude, discharge characteristics, and water residence time. For example, on the west coast the SW rivers drain red loamy soils in contrast to the NW rivers that drain black soils. However, on the east coast, the rivers have red loamy and alluvial soils in their upper and lower catchments, respectively except the Godavari and Krishna that supply black soils in their upper catchment, red loamy and alluvial soils in their middle and lower catchments, respectively (https://www.gsi.gov.in/). Changes in the source and nature of C impacts the subsequent fate of C in the estuary. The diversity of terrestrial, freshwater, and estuarine conditions across the Indian sub-continent makes it a particularly interesting setting to evaluate varying drivers of estuarine C cycling. This diversity merits a thorough review on the C biogeochemistry of Indian estuaries to highlight a holistic perspective of how Indian estuaries serve as an integral part of the global C balance. The general characteristics of the major Indian estuaries are presented in Table 1 and estuaries that have been included in this review are presented in Figure 1.

Material and methods

The dissolved and particulate C as well as trace gas (CO_2 & CH_4) data from the Indian estuaries were compiled and grouped according to the marginal sea they mix with (i.e., BB and AS). Similarly, data from wet (June – September; high freshwater discharge) and dry (pre-monsoon: February – May & post-monsoon: October – January; low freshwater discharge) seasons were pooled; the wet season has considerably more data than the dry. Thus, mean pre- and post-monsoon data were considered to be dry seasons to improve statistical rigor. All data collected from the literature were statistically reanalysed and redrawn based on differences in wet/dry season and marginal sea end member using Sigma plot Statistical Software V12. Statistical analysis showing $p < 0.05$ is considered statistically significant while $p > 0.05$ was considered not significant. To highlight general features of the Indian estuaries, estuaries having much scattered values compared to the others were excluded from our re-analysis (see figures). Additionally, we have reassessed, recalculated, and extrapolated the existing data wherever possible to extend quantitative understanding on C budgets of the Indian estuaries as well as its impact on global C budgets. All the data used in the paper is presented graphically in Fig. 2-6 and the correlations between parameters is presented in the supplementary file (see Fig. S1-S20).

Results

Salinity, dissolved oxygen, and pH variability

In the dry season for BB and AS estuaries, surface water salinity ranged from 3.86 to 23.91 (mean: 12.49 ± 6.85) and 0.23 to 22.84 (mean: 11.96 ± 6.81), respectively. During the wet season, salinity decreased more significantly in the AS estuaries (salinity: 0.04 – 7.32; mean: 1.49 ± 2.53; 88% decrease) than the BB estuaries (salinity: 0.09 – 28.78; mean: 10.83 ± 9.79; 13% decrease) (Fig.2A & 2B; Sarma et al., 2012; Rao et al., 2016; Dutta et al., 2015, 2019a, 2021; Samanta et al., 2015; Akhand et al., 2016; Ganguly et al., 2011; Pattanaik et al., 2017). High salinities in both seasons are also associated with high tides (Akhand et al., 2016; Dutta et al., 2019b).

Surface water %DO for the BB estuaries varied between 63 and 105% (mean: 93 ± 12%), 72 and 119% (mean: 95 ± 11%) during the wet and dry seasons, respectively, which is higher than in the AS (wet season: 74 – 95%, mean: 85 ± 8%; dry season: 63 – 98%, mean: 81 ± 10%) (Sarma et al., 2012; Rao et al., 2016; Dutta et al. unpublished data; Fig. 2C & 2D). Additionally, in vegetated wetlands bordering the estuaries, Dutta et al. (2019b) showed lower %DO in a pre-monsoon diurnal C study in the Saptamukhi estuary during low tide.

Coinciding with %DO, BB estuaries had higher surface water pH values (wet season: 6.66 – 8.61, mean: 7.77 ± 0.52; dry season: 7.96 – 8.33, mean: 8.15 ± 0.12) than in AS during both seasons (wet season: 5.98 – 7.51, mean: 6.84 ± 0.49; dry season: 7.23 – 7.90, mean: 7.70 ± 0.31) (Fig. 2E & 2F; Sarma et al., 2012; Rao et al., 2016; Dutta et al., 2015, 2019a, 2021; Samanta et al., 2015; Akhand et al., 2016; Ganguly et al., 2011; Pattanaik et al., 2017; Bouillon et al., 2003; Piplode and Barde, 2015; Sangani and Manoj, 2017). Regarding tidal

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influence, Dutta et al. (2019b) showed lower pH values during low tide in the Saptamukhi estuary.

DIC and δ^{13}C$_{DIC}$ variability

BB estuaries had higher DIC in surface water (862 – 4166 µM; peak in the Veller) compared to AS (280 – 837 µM) during the wet season. However, in the AS high DIC values have been reported for the following rivers that feed these estuaries: Narmada (2240 µM); Tapti (3484 µM); Sabarmati (1760 µM); and Mahisagar (1899 µM) (Sarma et al., 2012; Rao et al., 2016; Dutta et al., 2015, 2019a, 2021; Samanta et al., 2015; Akhand et al., 2016; Ganguly et al., 2011; Pattanaik et al., 2017; Piplode and Barde, 2015; Sangani and Manoj, 2017; Bhavya et al., 2017; Fig. 3A & 3B). On average, wet season DIC for the BB estuaries is ~47% higher than AS. For the dry season, the BB estuaries had comparatively higher DIC (1541 – 2954 µM; peak in the Hooghly) than AS (Kochi backwater = 1192 µM; Akhand et al., 2016; Dutta et al., 2019a, 2021; Gupta et al., 2009; Fig. 3A & 3B). The reported DIC values for the major Indian estuaries are relatively higher compared to other world rivers and estuaries (Table 2).

During the wet season, the AS estuaries showed wider variability of δ^{13}C$_{DIC}$ (-5.10 to -13.00‰; mean: -8.25 ± 2.70‰; peak at the Zuari and Bharatakulza) compared to BB (-2.14 to -7.90‰; mean: -4.18 ± 1.85‰; peak at Ponnayaar). During the dry season, δ^{13}C$_{DIC}$ varied between -5.07 and -3.24‰ (mean: -3.78 ± 0.86‰) in the BB estuaries with peak values in the Matla estuary (Fig. 3C & 3D; Dutta et al., 2019a, 2021; Krishna et al., 2019).

Distribution of DOC and POC

Mean surface water DOC concentration in the BB estuaries (239 – 1079 µM; mean: 418 ± 217 µM; peak in the Ambalayaar) was ~14% higher compared to the AS (37 – 716 µM, mean: 359 ± 172 µM; peak in the Tapti) (Krishna et al., 2015; Ganguly et al., 2011; Bouillon et al., 2003; Fig. 3E & 3F) during the wet season, while for the BB, DOC varied between 169 and 497 µM (mean: 322 ± 111 µM) with peak values in the Hooghly estuary (Dutta et al., 2019a, 2021; Fig. 3E). DOC values reported for the major Indian estuaries were generally higher compared to those reported for other estuaries worldwide (Table 3).

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The mean POC concentration for BB estuaries (51 – 480 µM; mean: 211 ± 142 µM; peak values in the Godavari River) were ~52% lower compared to the AS (68 – 750 µM, mean: 321 ± 245 µM; peak values in the Narmada River) (Sarma et al., 2014; Rao et al., 2016; Fig. 4A & 4B) during the wet season. However, the BB estuaries had ~45% higher POC (54 – 289 µM, mean: 117 ± 68 µM; peak values in the Hooghly estuary) than the AS (45 – 98 µM, mean: 64 ± 19 µM; peak values in the Bharatakulza) (Rao et al., 2016; Dutta et al., 2019a, 2021; Fig. 4A & 4B), during the dry season.

$\delta^{13}C_{POC}$ during the wet season varied between -30.40 and -23.40‰ (mean: -26.36 ± 2.41‰) for the BB estuaries with peak values observed in the Hooghly (Sarma et al., 2014; Dutta et al., 2019a, 2021; Ray et al., 2015, 2018; Fig. 4C). On average, the AS estuaries had ~1.33‰ lower $\delta^{13}C_{POC}$ values (-31.40 to -22.60‰; mean: -27.68 ± 3.02‰; peak in the Narmada; Fig. 4D) (Sarma et al., 2014). Dry season $\delta^{13}C_{POC}$ values for the BB varies between -23.96 and -23.38‰ (mean: -26.36 ± 2.41‰) with peak values in the Saptamukhi estuary (Dutta et al., 2019a, 2021; Ray et al., 2015, 2018; Fig. 4C).

Distribution of CO_2 and CH_4

pCO_2 during the wet season varied over a wide scale (BB estuaries = 248 - 15210 µatm; peak in the Godavari; AS estuaries = 37 - 716 µatm; peak values in the Tapti) compared to the dry season (BB estuaries = 355-1648 µatm) (Sarma et al., 2012; Dutta et al., 2019, 2021; Ganguly et al., 2011; Bouillon et al., 2003; Fig. 5A & 5B). On average, wet season pCO_2 for the BB estuaries was ~6 times higher than the dry season. pCO_2 values for the Indian major rivers are higher than those reported for other rivers worldwide (see Table 2). During the wet season, CH_4 concentrations in the BB and AS estuaries varied between 4 and 130 (mean: 32 ± 34 nM; peak values in the Ambalayaar river), 5 and 573 (mean: 176 ± 240 nM; peak values in the Netravathi River), respectively (Rao et al., 2016; Dutta et al., 2015, 2021; Fig. 6A & 6B). In the dry season, CH_4 concentrations in the BB and AS estuaries varied between 5 and 179 nM (mean: 44 ± 47 nM; peak values in the Vaigai River), 18 and 488 nM (mean: 100 ± 137 nM; peak values in the Tapti River), respectively (Rao et al., 2016; Dutta et al., 2015, 2021; Fig. 6A & 6B). On an average, the AS estuaries had ~5.5 and ~2.3 times higher CH_4 concentrations than the BB during the wet and dry seasons, respectively.

The observed range in CH_4 concentrations in Indian estuaries is mostly higher compared to that reported for most of the world's estuaries (Table 4).

Discussion

The Indian estuaries, where bi-carbonate is the dominant form of DIC (Dutta et al., 2019a), are oxic in nature and complete to partial DO undersaturation while transiting from the AS estuaries to the BB estuaries. The aerobic environment indicates the Indian major estuaries as hotspots for aerobic degradation of organic matter. Concurrently, in the vegetated coastal wetland, oxygen depleted porewater discharge from intertidal sediment to adjoining estuary results to low %DO during low tide (Dutta et al., 2015) when higher organic matter respiration adds H^+ to the estuary decreasing pH (Dutta et al., 2019b).Other work has shown a flux of sediment porewaters to the estuary "proper" during low tide (Dutta et al., 2013, 2017).

Sources, sinks, and drivers of DIC cycling

Estuarine DIC concentration and speciation is controlled by a variety of mechanisms including carbonate dissolution/precipitation, community metabolism, and air-water CO_2 exchange. Additionally, mixing, surface run-off, groundwater discharge, tidal characteristics (for vegetated wetlands), anthropogenic discharges, weathering of rocks, and climatic condition also influence the estuarine DIC pool. These mechanisms are discussed below in the context of observations made in Indian estuaries.

Chemical weathering, precipitation and physiography of Indian river basins

Carbonate mineral weathering has been shown to be an important contributor to the DIC pool of Indian estuaries based on observed $\delta^{13}C_{DIC}$ – TAlk relationships (significantly positive; $r^2 = 0.52$, $p < 0.01$; Krishna et al., 2019). Despite higher chemical weathering in the Deccan Trap basalts (Das et al., 2005; Singh et al., 2005) that occupied the catchments of north western rivers and upper reaches of the Godavari and Krishna, a larger DIC is reported in rivers draining over metamorphic rock landscapes. Additionally, despite higher weathering rates caused by heavy precipitation in the SW region of the Indian sub-continent (Gupta et

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al., 2011), lower DIC concentrations are reported there. This suggests alternate drivers of DIC behavior in this region, as discussed below.

Krishna et al. (2019) proposed the degree of precipitation as the major cause of low estuarine DIC levels based on the exponential decrease in DIC with precipitation (r^2 = 0.72). Our individual analysis of BB and AS datasets shows a significant relationship existing between wet season DIC and precipitation with linear and exponential relationships, respectively, for the two marginal seas (Fig. S1). This suggests that the variability of precipitation plays a an important, but varying role in controlling DIC in both BB and AS estuaries. DIC has also been shown to be positively correlated with the length of the rivers (r^2 = 0.38, $p < 0.01$; Krishna et al., 2019). Riverine DIC has been reported to increase along the course of the fluvial network (Hotchkiss et al., 2015) due to an increase in the residence time of water (Catalan et al., 2016). The comparatively smaller rivers draining into AS estuaries reduces the residence time of water, with less opportunity for organic matter to be remineralized to DIC (Krishna et al., 2019).

Estuarine mixing

DIC and $\delta^{13}C_{DIC}$ values generally increase linearly with increasing salinity in the Indian estuaries during both wet and dry periods (Fig. S2). However, the DIC – salinity relationship for BB estuaries fits well with a polynomial relationship for the wet season DIC at salinities >12 (Fig. S2A). These statistical analyses indicate that the degree of marine and fresh waters mixing plays a crucial role in regulating DIC budgets of Indian estuaries. The same was previously reported for the Hooghly estuary (Dutta et al., 2019a, 2021; Samanta et al., 2015) as well as Godavari estuary (Bouillon et al., 2003) from the Indian sub-continent. These studies applied a two-end member mixing model for these estuaries to quantitatively understand processes links with DIC addition/removal. Here, the proportional relationship between salinity and $\delta^{13}C_{DIC}$ is well explained based on the fact that $\delta^{13}C_{DIC}$ of marine water is greater than the $\delta^{13}C_{DIC}$ of freshwater. However, the proportional relationship between salinity and DIC despite the concentration of DIC of marine water being less than the concentration of DIC freshwater (Sabine et al., 2002; Sarma et al., 2012) suggests additional DIC inputs to Indian estuaries via other pathways discussed below.

Groundwater DIC discharge

Groundwater plays a pivotal role in regulating elemental concentrations as well as isotopic signatures of rivers and estuaries if they are fed by aquifers (Samanta et al., 2015). At the mouth of the Ganga–Brahmaputra system in Bangladesh, Moore (1997) reported the role of submarine groundwater discharge (SGD) on controlling the abundance and distribution of selected elements (e.g., Ba) and isotopes (e.g., ^{226}Ra). There are relatively few studies of SGD in Indian estuaries, but several recent datasets on groundwater DIC exist from the Indo-Gangetic basin. Previously, Samanta et al. (2015) reported a wide variability in shallow groundwater DIC concentrations (4.39 – 11.21 mM) and $\delta^{13}C_{DIC}$ (-13.3‰ to -2.3‰) from the surrounding regions of the Hooghly estuary. Dutta et al. (2019a) reported a similar range of values during a post-monsoonal study on Hooghly-Sundarbans systems (Hooghly: DIC = 5.66 – 11.76 mM, $\delta^{13}C_{DIC}$ = -12.66‰ to -6.67‰; Sundarbans: DIC = 7.52 – 13.60 mM; $\delta^{13}C_{DIC}$ = -18.05‰ to -6.84‰) covering the entire stretch starting from freshwater to marine regimes. In both cases, groundwater DIC concentrations were greater than surface water concentrations, suggesting that SGD is an important source of DIC to the Indian estuaries. Mixing calculations performed for the low salinity region of the Hooghly estuary suggest that SGD contributes to ~5 – 20% of the estuarine DIC pool, though these calculations were based on Ca and salinity, not direct DIC flux measurements (Samanta et al., 2015). Contrasting these findings, Somayajulu et al. (2002) found limited evidence for groundwater contribution in the Hooghly estuary based on 'radium' isotopes.

For vegetated coastal wetlands (e.g., mangroves, seagrass, and saltmarsh), exchange fluxes between sediment porewaters and estuarine surface waters play a significant role in regulating DIC budgets (Maher et al., 2013, 2016; Dutta et al., 2015; Tait et al., 2016; Bouillon et al., 2007). Dutta et al. (2019a) estimated porewater DIC levels in the Indian Sundarbans mangrove system to be 13.43 mM (~6 times higher than surface water DIC) with depleted $\delta^{13}C_{DIC}$ signatures (-18.05‰). The reported porewater DIC concentration in this mangrove system is much higher than other mangroves around the world (Bouillon et al., 2007; Taillardat et al., 2018; Maher et al., 2013). The porewater – surface water DIC exchange flux was estimated to be 770 mmol m^{-2} d^{-1} based on the DIC concentration

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gradient, porewater specific discharge, and porosity (Dutta et al., 2019a). Integrating this flux over the entire intertidal zone of the Indian Sundarbans mangroves (45% of total forest area; http:// www.sundarbanbiosphere.org/html_files/sunderban_biosphere_reserve.htm), total DIC export from intertidal mangrove sediments to the estuary is estimated to be ~6.37 Tg C yr^{-1}. Furthermore, Ray et al. (2018) estimated a DIC export from the estuaries of the Indian Sundarbans to the adjoining BB of ~3.69 Tg C yr^{-1}. Considering very limited anthropogenic inputs to the estuaries of the Sundarbans (Dutta et al., 2015), this calculation suggests that ~58% of total DIC export from the Sundarbans mangrove sediment is transported to the BB and the rest either increases estuarine DIC pools or is removed within the estuary via biogeochemical processes. DIC removal in the estuaries of the Indian Sundarbans is also evident during the post-monsoonal period when stable isotopic signatures suggest a large DIC output compared to input via mangrove-derived OC mineralization (Dutta et al., 2019a)

Anthropogenic DIC discharge

Although anthropogenic C fluxes are not reported for most of the Indian estuaries, the relationship between population density and DIC can be used as a proxy to examine anthropogenic influences (Krishna et al., 2019). Krishna et al. (2019) proposed significant anthropogenic contributions to estuarine DIC based on the linear relationship between population density and DIC (r^2 = 0.41, p <0.01 excluding the Sabarmati and Mahisagar estuaries). However, our data analysis separating BB and AS estuaries shows no significant relationship during the wet season (Fig. S3), suggesting limited anthropogenic influence on DIC. Our findings are supported by pre-monsoon measurements in the anthropogenically stressed Hooghly estuary (Dutta et al., 2021); although population density data was not available for this study region, both sides of the river bank are occupied by the very densely populated city including the megacity Kolkata as well as several jute and other industries that supplies 1154 million L^{-1} of anthropogenic discharge on a daily basis (Dutta et al., 2019a; Ghosh, 1973; Khan, 1995). Despite these large anthropogenic discharges, the study identified a predominance of estuarine algae and marine plankton in the POC pool of the Hooghly estuary and from that they proposed the anthropogenic organic C (i) either triggered productivity (but no evidence for increased productivity was observed), (ii) principally exists

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in the DOC phase, or (iii) if it exists principally as POC, its biogeochemical modification is happening in the particulate phase. These uncertainties highlight the need for detailed quantification of anthropogenic DIC fluxes to the Indian estuaries considering the widespread and ever-expanding human development and activities along the Indian coastline over the years.

Hydrological and biogeochemical drivers of DIC cycling

During the wet season, a significant positive relationship exists between $\delta^{13}C_{DIC}$ – DIC for the both BB and AS estuaries (Fig. S4). However, the relationship turns negative for the dry season in BB estuaries (Fig. S4A). The positive relationship during the wet season suggests that ^{13}C enriched DIC is exported to the estuaries, which is perhaps related to carbonate dissolution. Supporting this hypothesis, Samanta et al. (2015) showed calcite saturation index values less than 0 (i.e., calcite dissolution) for all monsoonal samples collected from the high saline region (salinity ≥ 10) of the Hooghly estuary. The negative relationship for BB estuaries during the dry season is perhaps caused by OM mineralization, as evidenced primarily by Bouillon et al. (2003) for the Godavari estuary and very recently by Dutta et al. (2021) for the Hooghly estuary during their pre-monsoonal surveys. Coinciding with this argument, Dutta et al, (2015) together with earlier studies by Mukhopadhyay et al. (2006), Biswas et al. (2007) showed that the Hooghly-Sundarbans system is net heterotrophic during the dry season (i.e., community respiration: productivity >1). Furthermore, based on the calculated ^{13}C value of respired C (Godavari = −28.6‰; Hooghly = −12‰) the authors proposed the potential role of estuarine algae ($\delta^{13}C$: − 12 to − 23‰; Smith and Epstein, 1971) and mangroves ($\delta^{13}C$: − 27‰; Miyajima et al., 2009) for DIC addition by respiration in the Hooghly and Godavari estuaries, respectively.

Despite a lack of $\delta^{13}C_{DIC}$ data unavailability for many of the Indian major estuaries, indirect relationships between different parameters as well as existing community metabolism data for some estuaries may also highlight the biological influence on DIC. AS estuaries with elevated phytoplankton levels (i.e., Chl *a* > 5 mg m^{-3}), Krishna et al. (2019) showed an indirect signature of phytoplankton productivity based on the negative DIC – Chl *a* relationship ($r^2 = 0.44$, $p < 0.01$). The same was again confirmed by the positive relationship

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between $\delta^{13}C_{DIC}$ and Chl *a* ($r^2 = 0.49$, $p < 0.01$) considering preferential ^{12}C uptake over ^{13}C leaves the residual DIC enriched in ^{13}C as during photosynthesis. Additionally, based on gross primary productivity and community respiration estimates by oxygen monitoring in light/dark bottles, Gupta et al. (2009) showed that the Cochin estuary was net autotrophic throughout the seasons (i.e., net DIC removal). However, contrasting conditions have been observed for the Mahanadi, Mandovi and Zuari estuaries. Pattanaik et al. (2019) estimated that the Mahanadi estuary was predominantly net autotrophic, whereas Ganguly et al. (2011) showed the same system to be net heterotrophic during the monsoon but fluctuated between net autotrophic and heterotrophic during the transition from pre- to post-monsoon periods. For the Mandovi and Zuari rivers, Ram et al. (2003) showed a transition from net autotrophy during the non-monsoon seasons to net heterotrophy during the monsoon season by the application of ^{14}C assimilation methods.

In addition to the aforementioned proxies, *n*DIC – *n*TAlk relationships have been used to identify the active biogeochemical processes in the surrounding estuaries near vegetated coastal wetlands. Previously, Dutta et al. (2019b) and thereafter Akhand et al. (2021) proposed the potential impact of denitrification, sulphate reduction and organic matter respiration in controlling DIC in the estuaries of the Sundarbans region based on the significant relationship between *n*DIC and *n*TAlk (Dutta et al., 2019b: $r^2 = 0.43$, $p < 0.05$, slope = 0.89). In addition, using the same approach, Borges et al. (2003) showed sulphate reduction together with organic matter respiration controlled DIC while investigating CO_2 dynamics in the mangrove-dominated Gaderu creek, India ($r^2 = 0.945$, slope: 0.61 ± 0.03). Indian mangrove systems appear to behave similar to Australian and Vietnam mangrove settings (Sippo et al., 2016). Considering the studied estuaries are all generally oxygenated, the anaerobic signals (as mentioned earlier) might be derived from the intertidal mangrove sediments during porewater exchange as proposed by Dutta et al. (2019b). This needs to be further examined for Indian coastal systems considering their diverse nature.

Sources, sinks, and drivers of DOC cycling

Estuarine DOC pools include both allochthonous and autochthonous origin (Ward et al., 2017). The major sources of allochthonous DOC are leaching of terrestrial OM (present in soils, debris of terrestrial plants, wood, and leaf litter) in the catchment area as well as localized inputs via anthropogenic discharges, which consists of both domestic and industrial sewages (Bin and Longjun, 2011; Ray et al., 2018; Dutta et al., 2019a). Precipitation (Sarma et al., 2014) together with tidal flushing (for vegetated wetlands) carry terrestrial DOC to rivers and subsequently to their estuaries (Dutta et al., 2019a, Maher et al., 2013). Autochthonous DOC sources include phytoplankton, autolysis of bacteria, bacteria and macrophytes, viral lysis of bacteria and phytoplankton, zooplankton grazing and excretion (Carlson et al., 1994; Bianchi et al., 2004; Bronk et al., 1994; Diaz and Raimbault, 2000; Fuhrman, 1999; Wilhelm and Suttle, 1999; Middelboe and Jorgensen, 2006; Berman and Bronk, 2003). Transformation of DOC through physical (e.g., flocculation and sorption/desorption), photochemical, and biological processes alter the signature of these DOC sources as they are transported through estuaries to the continental shelf (Ray et al., 2018, Dutta et al., 2019a, 2019b).

Terrestrial DOC fluxes

Terrestrial DOC fluxes normalized to catchment area (i.e., DOC yields) can vary by orders of magnitude. Krishna et al. (2015) calculated catchment area normalized fluxes of DOC to Indian estuaries during the dry season and it accounts for 35 to 1903 g C m^{-2} yr^{-1}. This is comparable to fluxes estimated for rivers around the world, which vary by an additional order of magnitude (0.1 – 5695 g C m^{-2} yr^{-1}; Alvarez-Cobelas et al., 2012).

For Indian estuaries, there was no significant relationship between DOC fluxes with freshwater discharge (r^2 = 0.01, p = 0.60) and catchment area of the river (r^2 = 0.05, p = 0.30), suggesting that these factors may not be the dominant control of terrestrial DOC fluxes in the region (Krishna et al., 2015). When we re-analysed BB and AS estuarine (Fig. 12A) data separately, catchment area and DOC fluxes remained uncorrelated (BB estuaries: r^2 = 0.17, p = 0.16; AS estuaries: r^2 = 0.18, p = 0.20; Fig. not shown). The earlier report together with our data analysis suggests variability of catchment area is not a major governing factor for DOC. However, DOC yield was strongly correlated with rainfall (r^2 = 0.87, p = 0.06), soil organic carbon content (r^2 = 0.94, p = 0.02), and biomass carbon (r^2 = 0.95, p = 0.02) (Krishna et al., 2015). Additionally, higher DOC fluxes were estimated for AS estuaries,

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which may be the result of intense DOC scrubbing from OC-rich soils by heavy rainfall during the SW monsoon (~3000 mm) (Soman and Kumar, 1990; Kishwan et al., 2009).

Groundwater DOC discharge

To our knowledge, no data is available for assessing the contribution of groundwater discharge to the DOC pools of Indian estuaries. Additionally, vegetated ecosystems along the coast add DOC to the adjoining estuaries through pore-water exchange, but no direct data is available on porewater mediated DOC export. However, indirect signatures of these fluxes have been observed. In the Pichavaram mangroves, SE coast of India, Ranjan et al. (2010) reported porewater DOC concentrations of 2071µM, which is higher than surface water values (166 – 1954 µM). The concentration gradient suggests that DOC export via porewater exchange more than likely occurs, but unfortunately a lack of other associated hydrological parameters needed to compute lateral exchange restricts us from calculating fluxes. Additionally, a diurnal study in the Indian Sundarbans by Dutta et al. (2019b) hypothesized that porewater mediated DOC exchange was the driver of ~ 30 µM higher average DOC concentrations during low tide compared to high tide.

Anthropogenic DOC discharge

The population density-DOC relationship shows distinct characteristics for the BB estuaries under population levels < 300 per km^2 and >300 per km^2. Under < 300 per km^2 the DOC – population density relationship showed a significant positive correlation (Fig. S5A). However, no significant relationship exists for population densities >300 per km^2 nor for the AS estuaries across the entire range of population densities (Fig. S5). This suggests limited anthropogenic impact on DOC in the Indian estuaries with the exception of BB systems with population densities less than 300 per km^2 (that includes Mahanadi, Vamsadhara, Nagavali, Godavari, Krishna, Penna, Ponnayaar estuaries). It is possible that anthropogenic inputs primarily influence POC pools, which is evident from $\delta^{13}C_{POC}$ values (see Fig. 4C & 4D). To properly understand the magnitude and impact of anthropogenic DOC inputs to Indian estuaries, more thorough investigations on $\delta^{13}C_{DOC}$ and other organic tracers of anthropogenic activity are needed.

Transformations driving non-conservative behaviour of estuarine DOC

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DOC generally behaves non-conservatively in Indian estuaries as evident from non-linear DOC – salinity relationships (Fig. S6A & S6B). These non-conservative behaviours have been previously reported by the Dutta et al. (2019a, 2019b, 2021) for the Hooghly-Sundarbans estuarine systems based on inter-spatial and diurnal variabilities. Krishna et al. (2015) showed no potential contribution of autochthonous DOC during the monsoon period based on its relationship with Chl *a* (r^2 = 0.004, p = 0.77). However, our dry season BB data analysis shows a significant link between DOC and Chl *a* (Fig. S6C) with an exponentially decreasing trend. This link suggests that unlike during the wet season, autochthonous DOC is an important source during the dry season DOC. The decreasing trend might be a signal of its simultaneous removal from the system considering algal-derived DOC is generally labile and may even promote priming effects that further degrade terrestrial DOC sources (Bianchi et al., 2015; Ward et al., 2016; 2019).

The mean DOC/DON ratio (8.4 ± 3.8) for Indian estuaries as calculated by Krishna et al. (2015) is close to the mean POC/PON ratio (8.7 ± 2) calculated by Sarma et al., (2014) and the biologically available DOC fraction in the global coastal ocean (8.8 ± 4.4) (Lonborg and Alvarez-Salgado, 2012). However, it is lower than that reported for the continental margins of the global oceans (DOC/DON = 17.8) (Lonborg and Alvarez- Salgado, 2012) and terrestrial refractory DOM (DOC/DON = 29.6) (Meybeck, 1982). Based on these ratios, Krishna et al. (2015) proposed that the DOC pool in Indian estuaries is primarily composed of high-quality non-refractory DOC.

The POC/DOC ratio can be used as a proxy to understand the impact of POC on DOC cycling. Based on the reported dataset, our calculated POC/DOC data for the BB estuaries (wet season: 0.55 ± 0.40; dry season: 0.36 ± 0.14) is relatively lower compared to the AS (0.82 ± 0.79 except for the Netravathi having a very high value of 10.8). Based on the differences between the two regions, we propose that POC-DOC conversion might be more active in the BB estuaries. However, this is the case for the BB only during the dry season when DOC increases with increasing POC (Fig. S7A). The opposite condition occurs during the wet season (Fig. S7A) and for the AS (Fig. S7B). This observation is similar to pre-monsoon spatial surveys in the Hooghly estuary (Dutta et al., 2021). Based on the DOC –

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POC relationship it was proposed that DOC removal via POC formation was more efficient than DOC formation via POC dissolution.

Regarding DOC photo-decomposition, no direct experiments have been conducted in Indian estuaries to our knowledge. However, diel measurements of day/night DOC variability suggest that photo-oxidation may have a limited influence on DOC levels in the Indian Sundarbans (Dutta et al., 2019b). It was hypothesized that unstable water conditions (Richardson number <0.14) leading to intensive vertical mixing with longitudinal dispersion coefficients of 784 m^2 s^{-1} limited the potential for photo-decomposition to occur (Sadhuram et al., 2005; Goutam et al., 2015).

Biological mineralization of DOC to CO_2 while transiting through the coastal ocean is another important pathway of DOC removal (Sarma et al., 2012; Dutta et al., 2019a). The DOC – pCO_2 relationship is not significant for the BB estuaries (Fig. S7C). For the wet season in AS estuaries, the nature of the DOC – pCO_2 relationship is different for pCO_2 < 6800 µatm and pCO_2 > 6800 µatm conditions. When pCO_2 is less than 6800 µatm, there is a significant positive relationship between DOC and pCO_2 in contrast to conditions when pCO_2 is greater than 6800 µatm and DOC shows a significant negative relationship with pCO_2 (Fig. S7D). The non-significant relationship for the BB during the wet season suggests that either there are limited DOC mineralization rates, or other key drivers of pCO_2 during this time. Dutta et al. (2019a) reported the same for the Hooghly estuary during the post-monsoon season. For the AS, a positive relationship between DOC and pCO_2 when pCO_2 is less than 6800 µatm suggests that DOC mineralization may be an important source of CO_2 to the system. However, the significant negative relationship under pCO_2 > 6800 µatm conditions suggests a decrease of aerobic bacterial activity with increasing DOC. In this case, another possibility is potential DOC mineralization and simultaneous removal of CO_2 by CO_2 outgassing (discussed later), primary productivity, carbonate precipitation, and/or export to the adjoining continental shelf.

Sources, sinks, and drivers of POC cycling

As with DOC, estuarine POC pools include both autochthonous and allochthorounous POC. Depending upon environmental conditions, the mixing between marine and fresh waters, inputs via terrestrial ecosystems, in situ biogeochemical processes, and anthropogenic inputs all contribute to the POC pool and mediate POC transformations.

Natural and anthropogenic POC sources

The stable isotopic composition of POC ($\delta^{13}C_{POC}$) is often used to identify sources of particulate organic matter in estuaries. The utility of this tracer can sometimes be diminished by high particulate loads and longer water residence times in certain Indian estuaries (Sarma et al., 2014); nonetheless it is the primary tool that has been used to evaluate POC origins in Indian tracers and there has been little use of other tools such as organic biomarkers in the region.

During the wet season, $\delta^{13}C_{POC}$ values across the Indian estuaries show dominant POC contributions from freshwater algae for both BB and AS estuaries, C_3 plant material for BB estuaries, and marine organic matter for AS estuaries (Fig. 4C & 4D). However, anthropogenic inputs are also evident during the dry season in the Hooghly estuary and the estuaries of the Sundarbans. Despite a wide range of cultivation of C_4 plants (e.g., Ragi, Bajra and Jowar) and C_3 plants (mostly wheat and rice) along the coast of the BB and AS, respectively, estuarine $\delta^{13}C_{POC}$ signatures are substantially different than $\delta^{13}C$ of these terrestrial plants. Regarding sewage contributions, the megacity Kolkata and some other highly populated cities (e.g., Howrah, North and South 24 Parganas) supply a large amount of municipal and domestic waste to the Hooghly estuary on a daily basis. The estuaries of Indian Sundarbans, on the other hand, have very limited anthropogenic discharges that mostly only occur during the monsoon (Dutta et al., 2015); the signature of these discharges can outweigh isotopic signatures of mangrove vegetation ($\delta^{13}C$ ~ -27‰; Miyajima et al., 2009) during this period. Population density and POC relationships are not significant for the BB or AS estuaries (Fig.S8), suggesting limited anthropogenic POC inputs to Indian estuaries. However, $\delta^{13}C_{POC}$ data clearly suggests anthropogenic POC contributions, especially for the BB (Fig. 4C & 4D). The contrasting findings between bulk and isotopic observations demands a comprehensive investigation on anthropogenic POC inputs to Indian estuaries, perhaps leveraging molecular biomarkers.

Biogeochemical drivers of POC cycling

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The relationships between POC and $\delta^{13}C_{POC}$ with salinity in Indian estuaries are not significant (Fig.S9). This suggests that freshwater mixing is not the major driver of POC composition or concentrations. Regarding aerobic mineralization, the relationship between $\delta^{13}C_{POC}$ and %DO are also not significant for the BB estuaries during both wet and dry seasons (Fig. S10A). In contrast to the BB, there was a significant negative relationship for the AS estuaries during the wet season (Fig. S10B). Our statistical analysis suggests that variability of %DO does not play an important role in POC transformations for the BB estuaries; however, contrasting reports exist regarding POC respiration in the Hooghly-Sundarbans system. During a post-monsoon survey, Dutta et al. (2019a) observed POC mineralization in freshwater regions of the Hooghly estuary as well as Sundarbans. But similar to these statistical analyses, a recent pre-monsoon study by Dutta et al. (2021) reported limited POC respiration in the Hooghly-Sundarbans systems. In contrast to the BB estuaries, the significant negative relationship in the AS suggests that aerobic POC mineralization plays an important role in transforming POC, which was also proposed by Sarma et al. (2012) when examining all Indian estuaries together. Our data analysis separating BB and AS datasets predicts only active POC respiration for the AS, which is also evident in pCO_2 trends.

Despite primarily oxygenated conditions in the surface waters of Indian estuaries, it is possible that anaerobic processes also transform and/or decompose POC, perhaps related to sediment transport and resuspension dynamics. For BB estuaries, there is a significant linkage between $\delta^{13}C_{POC}$ and CH_4 during both wet and dry seasons (Fig.S11A). The relationship might suggest CH_4 production via anaerobic POC degradation (methanogenesis), which was reported by Dutta et al. (2021) for the Indian Sundarbans. In contrast to the BB, there is an exponential relationship between $\delta^{13}C_{POC}$ and CH_4 in the AS, which may suggest some linkage between estuarine POC and CH_4 cycling dynamics (Fig. S11B).

Sources, sinks, and drivers of CO_2 cycling

Estuarine pCO_2 is principally controlled by community metabolism (i.e., balance between respiration and primary production) as well as carbonate precipitation and dissolution. In addition, hydrological (e.g., estuarine mixing and groundwater discharge) and physical (air-water CO_2 exchange) processes also control the level of variability of pCO_2.

Riverine CO₂ sources

Taking all Indian estuarine data together, Sarma et al. (2012) showed a significant positive relationship between wet season pCO_2 and river discharge ($r^2 = 0.71$; $p < 0.001$ excluding the largely anthropogenically stressed Tapti estuary). But our data analysis shows contrasting result when BB and AS estuaries are analysed separately. Excluding the Ponnayaar, the wet season pCO_2 - discharge relationship is significant and positive for the BB estuaries ($r^2 = 0.82$, $p < 0.001$; Fig.S12A). Low river discharge favours a higher proportion of marine water within the estuary, resulting in low pCO_2. However, there was no significant relationship between pCO_2 and discharge for AS estuaries (Fig. S12B).

Groundwater CO₂ sources

To our knowledge, no data exists to evaluate fresh groundwater contributions to estuarine pCO_2 for Indian estuaries. However, Akhand et al. (2021) reported porewater pCO_2 values up to 5423 µatm in the Indian Sundarbans mangroves. Using mean annual soil temperature and porewater salinity from Dutta et al., (2013), we estimate that this equates to a CO_2 concentration of 137 µM. By using porewater-specific discharge and porosity (Dutta et al., 2013, 2015), it is estimated that CO_2 export by porewater exchange with the adjoining river is ~ 7.89 mmol m^{-2} d^{-1}. This value is much lower compared to that reported for the North creek, New South Wales, Australia (1622 mmol m^{-2} d^{-1}; Atkins et al., 2013). Extrapolating the flux over the entire intertidal area of the Indian Sundarbans mangrove system, total CO_2 export flux via pore-water is calculated as 0.24Tg C yr^{-1}, which is ~3.8% of the total DIC export. This calculation suggests that pore-water DIC principally includes carbonate and bi-carbonate rather than CO_2.

Anthropogenic CO₂ sources

For the BB, pCO_2 shows a significant negative relationship with population density (Fig. S13A). However, the relationship is not significant for the AS estuaries (Fig. S13B). This analysis suggests that anthropogenic CO_2 inputs might impact pCO_2 in BB estuaries but not in the AS. The lack of a significant relationship with DIC (discussed earlier) together with

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pCO$_2$ decreasing with increasing population in the BB might be an indicator of removal of pCO$_2$ driven by anthropogenic inputs; for example, nutrient inputs may promote increased primary productivity and/or eutrophication.

Biogeochemical drivers of CO_2 cycling

During the wet season, pCO$_2$ shows a significant negative relationship with %DO in both the BB and AS estuaries (Fig.S14). The significant relationships suggest occurrence of a mechanism that produces CO_2 with simultaneous consumption of dissolved O_2 within the water column, i.e., organic matter mineralization. This relationship also holds up when analysing all Indian estuarine data together (Sarma et al., 2012; $r^2 = 0.56$, $p < 0.001$). Sarma et al., (2012) confirmed that organic matter mineralization drove this relationship based on the positive $[CO_2^*]_{Excess}$ – apparent O_2 utilization (AOU) relationship. AOU calculations were not possible for our compiled dataset of BB and AS estuaries, so we extracted data from Sarma et al. (2012) using a graph reading tool (http://www.graphreader.com/). Excluding two data points having maximum $[CO_2^*]_{Excess}$ and minimum AOU, respectively (marked in Fig. 21), the $[CO_2^*]_{Excess}$ and AOU slope for the major Indian estuaries is calculated as 2.43. This is much higher than the theoretical value for Redfield respiration ($\Delta CO_2/-\Delta O_2 = 0.90$; Zhai et al., 2005), suggesting higher wet season CO_2 production in the Indian estuaries than expected from Redfield respiration. However, the reverse case applies for the BB during the dry season when the pCO$_2$ - %DO relationship is not significant ($r^2 = 0.34$, $p = 0.22$; Fig.S14A), indicating limited impact of organic matter respiration on pCO$_2$. In this regard, during a post-monsoonal survey Dutta et al. (2019a) showed that organic matter respiration played a significant role in CO_2 production in the estuaries of Sundarbans but not in the Hooghly estuary. An opposite trend was reported during pre-monsoon season (Dutta et al., 2021).

Other than aerobic respiration, nitrification also plays a crucial role in increasing estuarine pH, which in turn favours greater CO_2 outgassing to the atmosphere (Billen, 1975, Frankignoulle et al., 1996). In these oxygenated estuaries, Sarma et al. (2012) showed higher NH_4^+ in the west coast rivers (1.4-16.6 mM) than the east coast rivers (0.2-7.0 mM). Although Miranda et al. (2008) hypothesized that it is unlikely that nitrification could be an important mechanism for mitigating NH_4^+ pollution in the Kochi Backwaters (drains into the

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AS), they estimated nitrification rates between 0.06 and 166 nmol N L^{-1} hr^{-1} there. Additionally, a recent study by Dutta et al. (2019b) also revealed that nitrification played an important role in the estuaries of the Indian Sundarbans based on the very high diurnal $\delta^{15}N_{PN}$ (8.71–14.75‰) compared to other Indian estuaries (northern rivers: 0.7 - 5.8‰, southern rivers: 5 - 10.3‰; Sarma et al., 2014). Preferential ^{14}N uptake during nitrification (Mariotti et al., 1984) results in ^{15}N enriched NH_4^+ pool, which in turn results to higher $\delta^{15}N_{PN}$ when incorporated by algae (Mariotti et al., 1984) and heterotrophic bacteria (Middelburg and Nieuwenhuize, 2000). The limited amount of work on nitrification in Indian estuaries suggests that it may play a role in pCO_2 cycling, but more systematic studies are essential to fill up the data gap in this topic.

Air-water CO_2 exchange

The flux of CO_2 to the atmosphere (FCO_2) during the wet season varies between -0.02 to 96.32 and 3.24 to 362.45 mmol m^{-2} d^{-1} for the BB and AS estuaries, respectively (Fig. 5C & 5D). In contrast, during the dry season FCO_2 is substantially lower (BB estuaries: -4.67 to 30 mmol m^{-2} d^{-1}; AS estuaries: 1.30 – 2.50 mmol m^{-2} d^{-1}). Positive and negative values (net emission and uptake, respectively) for the BB estuaries suggest that the estuaries act as both CO_2 sources and sinks. The AS estuaries, on the other-hand, are persistent CO_2 sources to the atmosphere. The negative FCO_2 values for BB estuaries are mostly associated with the Rushikulya during the wet season and major estuaries of the Indian Sundarbans during the dry season.

CH_4 dynamics in Indian estuaries

General sources and sinks of CH_4

In the anoxic environment, CH_4 produces in the terminal step of the organic matter decomposition when all the electron acceptors consume and electron donors are surplus (Dutta et al., 2017). The produced CH_4 enters in the estuaries by lateral transport from the upstream river and inputs from the sediments via diffusion and groundwater discharge. However, the removal of CH_4 includes aerobic, anaerobic oxidations and outgassing to the regional atmosphere. In addition to this, stratification of water column also promotes CH_4 production (Rao et al., 2016).

Riverine CH_4 sources

In the Indian estuaries, CH_4 - discharge relationships are not significant (Fig. S16) excluding the AS during the dry season where the relationship is significant (Fig. S16B). This statistical analysis suggests that freshwater discharge only plays a major role in controlling the concentration of CH_4 in the AS estuaries during the dry season. An inverse relationship between CH_4 and salinity has also been reported for estuaries worldwide (Zhang et al., 2008; Middelburg et al., 2002; Koné et al., 2010; Bange, 2006; Borges et al. 2015), which is associated with oxidation and outgassing removing freshwater-derived CH_4 along the estuarine gradient.

Groundwater CH_4 sources

Groundwater discharge is considered to play a pivotal role in controlling CH_4 budgets in estuaries, particularly in mangrove dominated estuaries (Dutta et al., 2015). Biswas et al. (2007) reported porewater CH_4 concentration of 5769 nM in the Indian Sundarbans. After almost a decade, in the same ecosystem Dutta et al. (2015) reported porewater CH_4 concentrations in intertidal (1881 – 3370 nM) and subtidal (2070 ± 1039 to 3980 ± 1227 nM) sediments, which had significantly higher concentrations than surface waters (54 ± 5 to 91 ± 21 nM). The concentration gradient results in advective and diffusive CH_4 fluxes on the order of 116 ± 31 to 199 ± 48 μmol m^{-2} d^{-1} and 7 ± 2 to 10 ± 2 μmol m^{-2} d^{-1}, respectively. Extrapolating these fluxes over the entire Indian Sundarbans it was estimated that groundwater contributed ~1.88 Gg CH_4 yr^{-1} to surrounding estuaries, ~99% of which advective flux via porewater exchange across the intertidal sediment-river interface (Dutta et al., 2015). Additionally, Rao et al. (2016) reported mean ground water CH_4 concentrations for the Godavari and Krishna estuaries of 1566 ± 81nM. The same study estimated groundwater - estuary advective CH_4 fluxes during the dry season of 19.2 and 22.4 μmol m^{-2} d^{-1} in the Godavari and Krishna rivers, respectively. However, sediment-water CH_4 fluxes were reported as 20.9 ± 3 and 25.1 ± 4 μmol m^{-2} d^{-1} in the Godavari and Krishna rivers, respectively. The author also proposed that ~40% of the CH_4 budget in the Godavari and

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Krishna estuaries was driven by the above-mentioned pathways. Groundwater CH_4 fluxes have not been studied in most of the other Indian estuaries, meriting a comprehensive investigation for future CH_4 budgets for Indian estuaries.

Anthropogenic CH_4 sources

Wastewater end member CH_4 data has not been studied for the major Indian rivers and estuaries. Alternatively, CH_4 – population density relationships can be used as a proxy to understand the impact of anthropogenic inputs. The relationships showed limited significance of anthropogenic inputs on CH_4 concentrations in the Indian estuaries (Fig.S17) but this should be confirmed by stable isotopic analysis of CH_4 as well as quantification of CH_4 concentrations in wastewater inputs.

Biogeochemical drivers of CH_4 cycling

The significant link between POC and CH_4 in Indian estuaries was previously discussed. In terms of methane oxidation, the oxygenated waters of Indian estuaries can only support aerobic CH_4 oxidation. Dutta et al. (2015a) reported CH_4 oxidation rates in the Indian Sundarbans (12.96 ± 2.86 to 30.22 ± 6.46 nmol L^{-1} d^{-1}), but the process might not influence CH_4 distribution significantly except for the AS during the wet season as evident from the CH_4 - %DO relationships (Fig. S18). During aerobic oxidation, CH_4 converts to CO_2 (Dutta et al., 2017). In the case of AS during the wet season, the CH_4 - pCO_2 relationship was positive and significant; in our other analyses there were not significant relationships except for a negative relationship between CH_4 and pCO_2 for BB during the dry season (Fig.S19). The significantly positive CH_4 - pCO_2 relationship during the wet season might be linked to similar sources of CH_4 and pCO_2 as previously proposed by Borges and Abril (2011). However, during the dry season, the significant negative CH_4 - pCO_2 relationship might be linked with CH_4 oxidation (which is not evident from the CH_4 - %DO relationship). As previously mentioned, investigation of the stable isotopic composition of CH_4 is needed to understand how important CH_4 oxidation is on the distribution of CH_4 in Indian estuaries. Additionally, methanogenesis may also be linked with water column stratification (Koné et al., 2010; Borges and Abril, 2011). In the Indian estuaries, salinity stratification is reported only during the dry season but it remains active for a small-time span (~2 – 3 weeks) as evident from daily observations in the Godavari (Sarma et al., 2010), Mandovi and Zuari (Pedneker et al., 2011), and Krishna estuaries (Dr. T.R. Kumari personal communication, 2016). Thus, methanogenesis in Indian estuaries is likely not principally linked with stratification (Rao et al., 2016).

Dams and reservoirs are considered a hotspot for methanogenesis. During the initial phase of reservoir construction (e.g., first decade), CH_4 inputs to the river and subsequently to estuaries can be substantial (Abril, et al., 2005; Kemenes et al., 2007; Kemenes et al., 2011; Barros et al., 2011). Several dams have been constructed in Indian rivers that store water for over 6 months (January to June) to meet irrigation, hydropower generation and domestic needs (Rao et al., 2016). Rao et al. (2016) reported ~3 times higher CH_4 levels during the storage period, indicating significant CH_4 production during this time. Monsoonal CH_4 concentrations in the Godavari estuary of 72 nM have been reported, which is close to that of discharge water from the upstream river (73 ± 10 nM; Rao et al., 2016). Additionally, our analysis shows a positive relationship between CH_4 concentration and the number of dams (Fig. S20), suggesting dams and reservoirs may substantially influence the CH_4 budget of Indian estuaries.

Air-water CH_4 exchange

During the wet season, the flux of CH_4 (FCH_4) in the BB estuaries varies between 0.01 and 11.80 µmol m^{-2} d^{-1} (mean: 2.93 ± 4.10 µmol m^{-2} d^{-1}; peak in the Ponnayaar). Wet season FCH_4 in the AS estuaries is ~13 times higher (0.11 – 299 µmol m^{-2} d^{-1}; peak in the Tapti estuary) than BB estuaries. However, the dry season shows a contrasting trend with higher fluxes in the BB estuaries (BB estuaries: 0.08 – 156 µmol m^{-2} d^{-1}, peak in the Matla estuary; AS estuaries: 0.30 – 29.30 µmol m^{-2} d^{-1}, peak in the Kochi Backwaters). Positive fluxes occur throughout both the wet and dry seasons suggesting that the Indian estuaries are persistent sources of CH_4 to the atmosphere.

Contribution of Indian estuaries to global C budgets

Impact on marine C budgets

A schematic diagram presenting dissolved and particulate C fluxes to/from the Indian estuaries is presented in the Figure 7. Krishna et al. (2015, 2019) quantified DIC and DOC export fluxes from Indian estuaries to the northern Indian ocean of ~10.30 Tg C yr^{-1} (~76% discharges via the BB estuaries) and 2.37Tg yr^{-1} (~30% higher export by BB estuaries than AS), respectively. Integrating DIC and DOC export fluxes, total dissolved C export via BB and AS estuaries to the northern Indian ocean is ~12.67 Tg C yr^{-1} of which ~81% is DIC. From a global perspective, a compilation of current global riverine C export to the ocean is presented in Table 5. We estimate average global riverine DIC and DOC exports to the ocean of 393 Tg C yr^{-1} and 218 Tg C yr^{-1}, respectively, for a total dissolved C export of 611 Tg C yr^{-1}. Indian rivers constitute ~1.3% of global freshwater discharge; the BB and AS cumulatively contribute 2.62% and 1.09% to global riverine DIC and DOC export to the ocean, respectively. This contribution is much lower compared to South American and African rivers (~17% and ~21% for DIC and DOC, respectively) draining into the Tropical Atlantic Ocean (Araujo et al., 2014). In total, the BB and AS estuaries contribute 2.07% of global total dissolved C export to the ocean. The Indian rivers contribute more DIC export relative to discharge compared to other global rivers (Table 5). The higher DIC flux from the Indian estuaries links with relatively significant silicate and carbonate mineral weathering rates in their drainage basins (Gurumurthy et al., 2012; Pattanaik et al., 2013) which in turn is a function of variability in lithological characteristics and climatology (Huang et al., 2012).

Vegetated coastal wetlands in the Indian subcontinent also play a significant role in coastal ocean C dynamics. Despite the Indian mangroves covering only ~4% of global mangrove surface area, C export fluxes from most of the mangroves surrounding estuaries are not available to precisely understand their impact on the oceanic C budget. In the Indian Sundarbans, Ray et al. (2018) reported total DIC and DOC export from the Indian Sundarbans to the BB of ~3.69 and 3.03 Tg C yr^{-1}, respectively, for a total of 6.72 Tg C yr^{-1}. The exported DIC from the Indian Sundarban mangroves is ~47% of total DIC export from the BB, highlighting the large role of the Indian Sundarbans in the DIC budget of BB. However, the fact that DOC export from the Sundarbans is greater than DOC export from BB estuaries (~1.34 Tg C yr^{-1}) suggests that substantial amounts of DOC are removed in transit from the Sundarbans estuaries to the continental shelf region and eventually to the northern Indian Ocean. On the other hand, it is possible that current C export flux estimates have large

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inaccuracies. For example, for the Sundarbans mangroves, literature-based discharge data was used to calculate the export flux rather than real time data. Regarding POC export, there are not enough observations of POC export fluxes to accurately calculate total export by Indian estuaries to the ocean.

Impact on atmospheric C budget

Despite having higher pCO_2 and CH_4 concentrations than other world rivers, we estimate lower air-water fluxes for the Indian rivers (Tables 1 & 4). This suggests that gas transfer velocities in the region are generally lower (which is a function of the wind speed over 10 m height of the river, water temperature, and salinity).

Sarma et al. (2012) calculated the total area of the Indian estuaries (consisting of 14 major, 44 medium and 162 minor estuaries) to be ~27000 km^2. Integrating the annual mean FCO_2 (22.41 mmol m^{-2} d^{-1}) and FCH_4 (20.76 µmol m^{-2} d^{-1}) based on the data compiled here to the entire surface area of the Indian estuaries, total CO_2 and CH_4 emissions from the estuaries of the Indian sub-continent are estimated to be ~9718 Gg C yr^{-1} and 3.27 Gg C yr^{-1}, respectively. Our recalculated gas flux estimates from the Indian estuaries are ~28% lower and ~19% higher for pCO_2 and CH_4, respectively, compared to previous estimates by Sarma et al. (2012) and Rao et al. (2016). Indian estuaries cover ~2.54% of the global estuarine surface area and contribute ~0.67% and ~0.12% to global CO_2 and CH_4 outgassing, respectively (Table 6). These estimates suggest a limited contribution of Indian estuaries to global estuarine CO_2 and CH_4 fluxes. In terms of anthropogenic greenhouse gas emissions, India emits 2.8 Gt CO_{2eq} annually of which 79%, 14%, and 5% are contributed by CO_2, CH_4, and N_2O, respectively (Government of India, 2018 Second Biennial Update Report to the United Nations Framework Convention on Climate Change "India: Third Biennial Update Report to The United Nations Framework Convention on Climate Change". Archived (PDF) from the original on 2021-02-27). Thus, emissions of CO_2 and CH_4 from the Indian estuaries only represent ~0.44% and ~0.002% of total Indian anthropogenic C emissions. In this regard, Frankignoulle et al. (1998) estimated CO_2 fluxes from European estuaries of 30 – 60 Tg C yr^{-1}, which is ~5 to 10% of total European anthropogenic emissions in 1995. This

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suggests that despite having ~17% of the global population, the Indian estuaries minutely contribute to atmospheric C budgets.

Mangroves are both a large sink (i.e., soil C burial) and source of greenhouse gases to the atmosphere (Chauhan et al., 2008; Krithika et al., 2008; Dutta et al., 2013, 2015, 2017; Barnes et al., 2011; Biswas et al., 2007; Akhand et al., 2021). Compiling a large mangrove dataset in the east coast of India, Banerjee et al. (2014) estimated mean CO_2 and CH_4 fluxes from the mangrove surrounding water to be 20.18 mol m^{-2} yr^{-1} and 0.027 – 17502 mmol m^{-2} yr^{-1}, respectively. The area of water surrounding mangroves is not well defined in India, but surface waters surrounding mangrove systems generally have lower CO_2 emission in contrast to the higher CH_4 emissions compared to fluxes reported here for the Indian estuaries.

To quantitatively understand the potential impact of riverine CO_2 and CH_4 emissions on regional climate change scenarios, standard procedure is to report gas emissions in tons of CO_2 equivalents, which is a universal unit of measurement used to indicate the global warming potential of a greenhouse gases, expressed in terms of a global warming potential of one unit of CO_2 (http://www.defra.gov.uk/enviornment/economy/reporting/). Additionally, it is important to consider the impact of gas emissions over both 20 year and 100 year time scales as sources and sinks can vary considerably over decadal timeframes (Kirschke et al., 2013, Neubauer and Megonigal, 2015), whereas C sequestration estimates may be better represented over 100 year time frames (Gatland et al., 2014). The global warming potential for atmospheric CH_4 is 56 and 21 times higher compared to the CO_2 over 20- and 100-years' time horizon, or 96 and 45 times higher than CO_2 if considering sustained-flux global warming potential (Neubauer and Megonigal, 2015). Using the former values, the global warming potential of Indian estuaries via cumulative emissions of CO_2 and CH_4 is calculated as ~9.90 x 10^6 and 9.79 x 10^6 Ton CO_2-eq for the 20- and 100-year time horizons, respectively, of which CH_4 contributes only ~1.85% and ~0.70%, respectively. Our review has highlighted the major governing factors of estuarine C cycling from the Indian sub-continent qualitatively. However, more detailed and mechanistic observations of the processes involved in estuarine C cycling is essential for more precise drafting of Indian estuarine C budgets, which is intricately linked with the global C cycle in a broader sense.

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Conclusion

In this review paper, data for 20 BB and 12 AS estuaries were compiled and reanalysed based on changes in season and marine end members to explore the mechanisms driving estuarine C biogeochemistry in India. The DIC in Indian estuaries is controlled cumulatively by geochemical (carbonate weathering), climatological (degree of precipitation), and hydrological (mixing) factors. Biogeochemically, carbonate dissolution and organic matter respiration control the DIC levels in the Indian estuaries. DOC behaves mostly non-conservatively and DOC - POC interconversion together with DOC mineralization appear to be major drivers for DOC cycling. POC is composed of freshwater algae, C_3 plant material, marine organic matter along with anthropogenic inputs in some eastern Indian estuaries. Respiration and methanogenesis appear to play a pivotal role in controlling POC. The pCO_2 is controlled principally by respiration with freshwater discharge only in the BB, however, POC together with methanotrophy and the abundance of dams control CH_4. FCO_2 estimates showed that AS is a persistent CO_2 source to the atmosphere, however, the BB varies between a source and sink. FCH_4 estimates show that Indian estuaries are a CH_4 source throughout both the AS and BB. From a global perspective, the Indian estuaries contribute 2.62% and 1.09% to global riverine DIC and DOC exports to the ocean, respectively. The total CO_2 and CH_4 flux from the Indian estuaries to the atmosphere are estimated as ~9718 Gg yr^{-1} and 3.27 Gg yr^{-1}, which contributes to ~0.67% and ~0.12%, respectively, to the global estuarine emissions estimates. Based on the present review, we suggest that a more through investigation on the mechanisms controlling C cycling (including rate quantification) in Indian estuaries is very essential to fill up the data gap in this area of research and also to more precisely draft the C budget of the estuaries around the Indian subcontinent.

Data availability

All the data used in the paper is adopted from the literature and the authors are thankfully credited. Moreover, the data has been presented graphically in the Fig. 2-6.

Author contribution

MKD: Designed the paper, analysed data and wrote first draft of the paper; KS and DP: Designed the paper and reviewed the first draft; NDW, TSB and DP: Edited and reviewed the final version.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1: General characteristics of major Indian estuaries.

Marine End member	Name of the estuaries	No of dams	Populations (per km^2)	Mean annual discharge (m^3 s^{-1})	Tidal amplitude (m)	Annual mean precipitation (mm)	Catchment area (x 10^3 km^2)
Bay of Bengal	Haldi	*	*	1600	7.01	1582	*
	Hooghly	*	*	1751	*	1582	60
	Saptamukhi	*	*	*	*	*	*
	Thakuran	*	*	*	*	*	*
	Matla	*	*	*	*	*	*
	Subarnarekha	12	338	392	*	1800	29.2
	Baitarani	8	324	903	*	1450	14.2
	Rushikulya	13	360	61	*	1000	9
	Mahanadi	280	282	2121	2.82	1406	141.6
	Dhamra	*	*	*	*	*	*
	Vamsadhara	3	130	113	*	1400	11
	Nagavali	4	150	64	2.17	1000	9.4
	Godavari	978	193	3505	2.1	1300	313
	Krishna	736	260	2213	1.98	784	259
	Penna	61	186	200	*	510	186
	Veller	3	457	29	1.51	980	457
	Ponnayaar	4	291	51	*	969	291
	Cauvery	122	393	677	*	1075	393
	Ambalayaar	*	*	28	*	*	*
	Vaigai	2	499	36	*	850	7
Arabian Sea	Kochi Back water	*	*	391	1.34	*	*
	Chalakudi	6	*	60.88	*	3600	1.7
	Bharatakulza	13	*	161	*	2500	6.2
	Netravathi	*	103	351	*	3923	3.2
	Sharavathi	3	109	144	*	4000	3.6
	Kali	6	111	152	*	3200	4.2
	Zuari	3	92	103	2.7	3500	1
	Mandovi	2	62	105	2.7	3500	3.6
	Narmada	281	184	1447	10.9	1120	99
	Tapti	375	208	472	*	888	65
	Sabarmathi	62	1702	120	*	787	21.7
	Mahisagar	138	507	349	7.63	785	34.8

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Table – 2: The DIC contents in some of the major estuaries of the world.

Rivers	DIC (µM)	pCO_2 (µatm)	FCO_2 (mmol m^{-2} d^{-1})	References
Mississippi	540	1335	270	Li et al., 2013
Amazon	**	4350	189	Richey et al., 2002
Hudson	**	1125	1637	Li et al., 2013
Yangtze	1700	1297	14.2	Wang et al., 2007
St. Lawrence	460	1300	78-295	Li et al., 2013
Xi river	1580	2600	190-357	Yao et al., 2007
Ottawa	50-300	1200	81	Telmar et al., 1999
Mekong	1590	1090	195	Li et al., 2013
Maotiao	2600 – 3020	3740	295	Wang et al., 2011
Pearl River	1850 - 3329	168-8364	-25.82 – 2293.58	Guo et al., 2008, 2009
Artic rivers	642-1792	**	**	Tank et al., 2012
Tyne	1208-3867	**	**	Baker and Inverarity (2004)
Ouseburn	2592 - 5317	**	**	Baker (2002)
River Tern	1742-3242	**	**	Cumberland and Baker (2007)
Columbia	**	176-735	-53 – 193.2	Evans et al. 2013
Indian estuaries	**280-4166**	**248-15220**	**-4.67 – 96.32**	**This review work**

**Data not available

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Table – 3: The DOC contents in some of the major estuaries of the world.

Rivers	DOC (µM)	References
Amazon Mainstream	300	Richey et al., 1990
St. Lawrence	313	Pocklington and Tan, 1987
Elbe	325-500	Ludwig et al., 1997
Nile	246	Abu el Ella., 1993
Columbia	177	Damn et al., 1981
Yellow river	267-708	Zhang et al., 1992
Rone	144	Kempe et al., 1991
Delware and Hudson	12.9 - 46.4	Seitzinger and Sanders, 1997
Mississippi	489	Bianchi et al., 2001
Ganga-Brahmaputra	323	Safiullah et al., 1987
Congo	604	Probst and Suchet, 1992
Yangtze	167 - 842	Zhang et al., 2005
Rioni	88	Romankevich and Artemyev, 1985
Seven	258 - 650	Mantoura and Woodward, 1983
Niger	309	Martins and Probst, 1991
Artic rivers	7.9 - 65	Holmes et al., 2012; Letscher et al., 2013
Indian estuaries	**37 - 1079**	**This review work**

*Mentioned earlier; **Data not available

Table – 4: The CH_4 fluxes in some of the major estuaries of the world.

Rivers	CH_4 (nM)	FCH_4 (µmol m^{-2} d^{-1})	References
Pearl River estuary	7-174	63.5	Zhou et al., 2009
Tyne	13-654	**	Upstill-Goddard et al., 2000
European estuaries	2-3600	130	Middelburg et al., 2002
Humber	16-669	**	Upstill-Goddard et al., 2000
Hudson	50-940	350	De Angelies and Scranton, 1993
Brisbane	31 - 578	19-1725	Musenze et al., 2014
Danube	131	470	Amouroux et al., 2002
Yangtze	13-27	35-144	Zhang et al., 2008
Bodden	2.4-370	30-210	Bange et al., 1998
Ivory Coast	**	25-1187	Kone et al., 2010
Choptank river estuary	**	2400	Lipschultz (1981)
Rhine and Scheldt	2.5-370	6-600	Scranton and McShane (1991)
Tomales Bay	8-100	7- 10	Sansone et al. (1998)
Temmesjoki estuary	240-506	**	Silvennoinen et al. (2008)
Randers Fjord estuary	41-420	70-410	Abril and Iversen (2002)
Rio San Pedro,	12-87	34-150	Ferrón et al. (2007)
Artic rivers	**	80-1020	Kling et al., 1992
Indian estuaries	**4 - 573**	**0.01-299**	**This review work**

**Data not available

Table – 5: Contribution of Indian estuaries to global estuarine C export to the ocean. The table is modified after Li et al. (2017). Values given here are in Tg yr^{-1} unit. *Data not available; **Calculation not possible; TDC = Total dissolved C, TPC = Total particulate C, TC = Total C, C_{DIC} = Contribution of DIC in TDC.

Export flux	Meybeck (1982, 1987)	Luwding et al. (1996a, b)	Harrison et al. (2005); Beusen et al. (2005)	Cai (2011)	Li et al. (2017)	Mean global riverine C export	Export from (BBE + ASE)	Global contributions by (BBE + ASE)
DIC_{Export}	430	320	*	410	410	393	10.30	2.62%
DOC_{Export}	220	210	170	250	240	218	2.37	1.09%
TDC_{Export} = (DIC + DOC) $_{Export}$	**650 (C_{DIC} ~66%)**	**530 (C_{DIC} ~60%)**	**	**670 (C_{DIC} ~61%)**	**650 (C_{DIC} ~63%)**	**611 (C_{DIC} ~64%)**	**12.67 (C_{DIC} ~81%)**	**2.07%**
POC_{Export}	180	170-190	200	220	240	204	*	**
PIC_{Export}	170	170	*	170	170	170	*	**
TPC_{Export} = (PIC + POC) $_{Export}$	350	~350	**	390	410	374	**	**
Total C export = (TDC + TPC) $_{Export}$	1000	880	**	1050	1060	985	**	**

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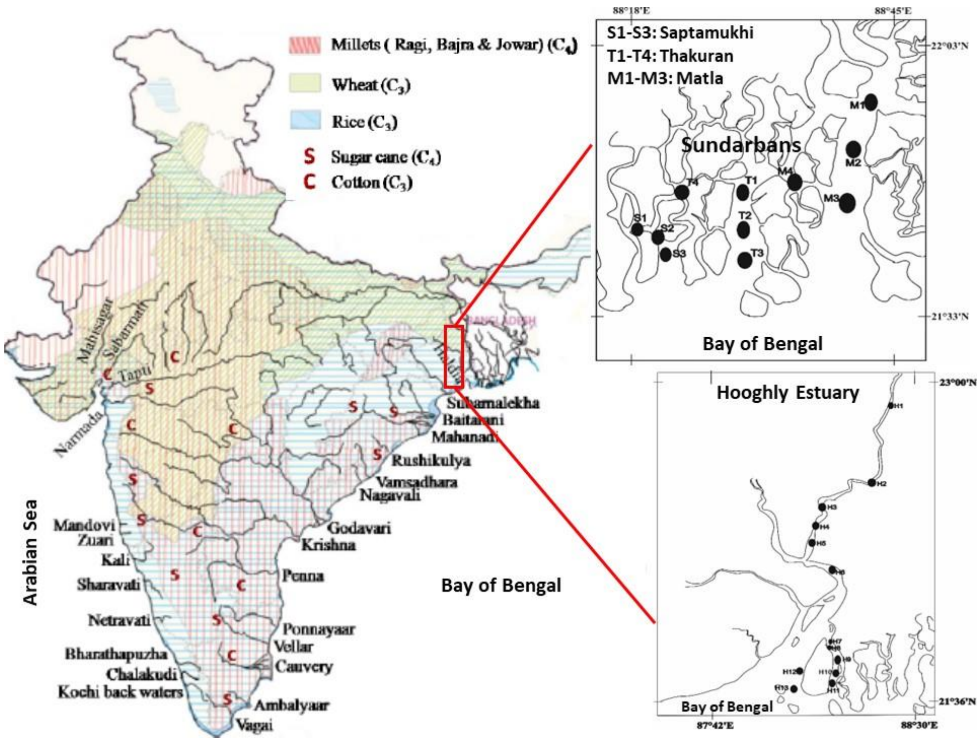

Fig. 1: Locations of the major estuaries of India. Modified from Sarma et al. (2012) and Dutta et al. (2019a).

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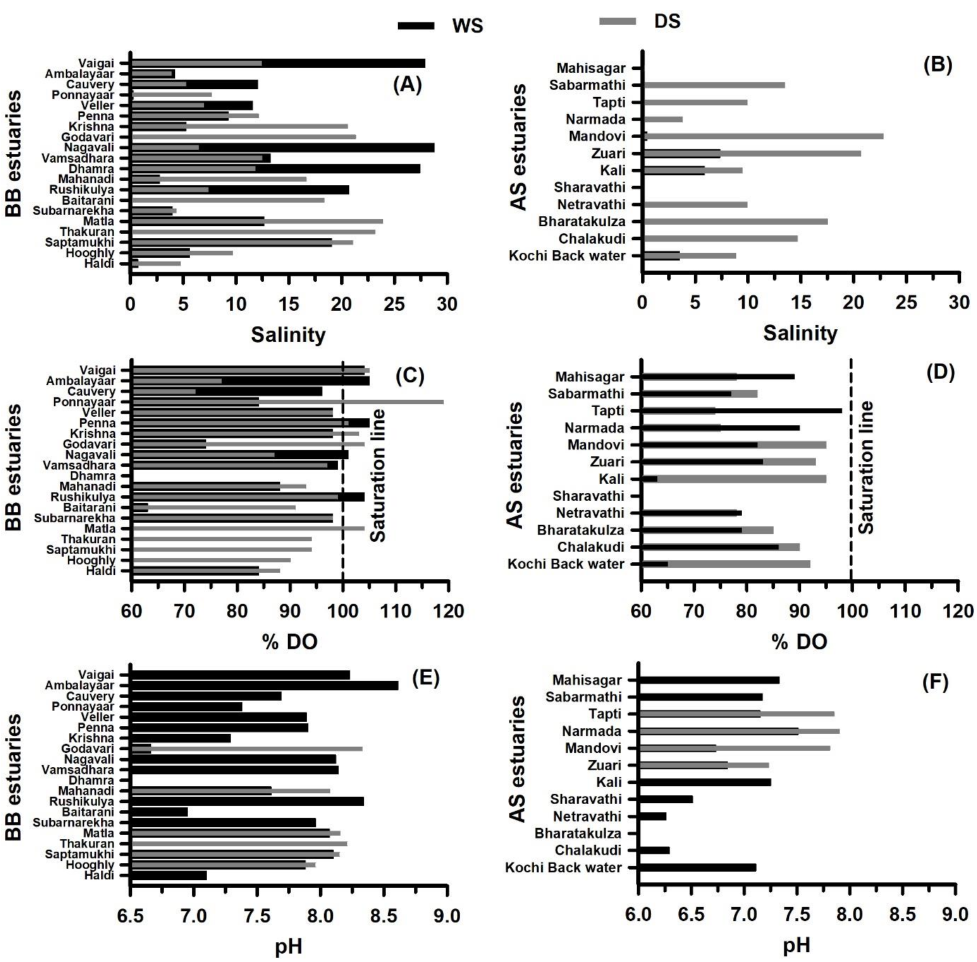

Fig. 2: (a) Salinity, (b) %DO, and (c) pH for the major Indian estuaries. WS = wet season; DS = dry season

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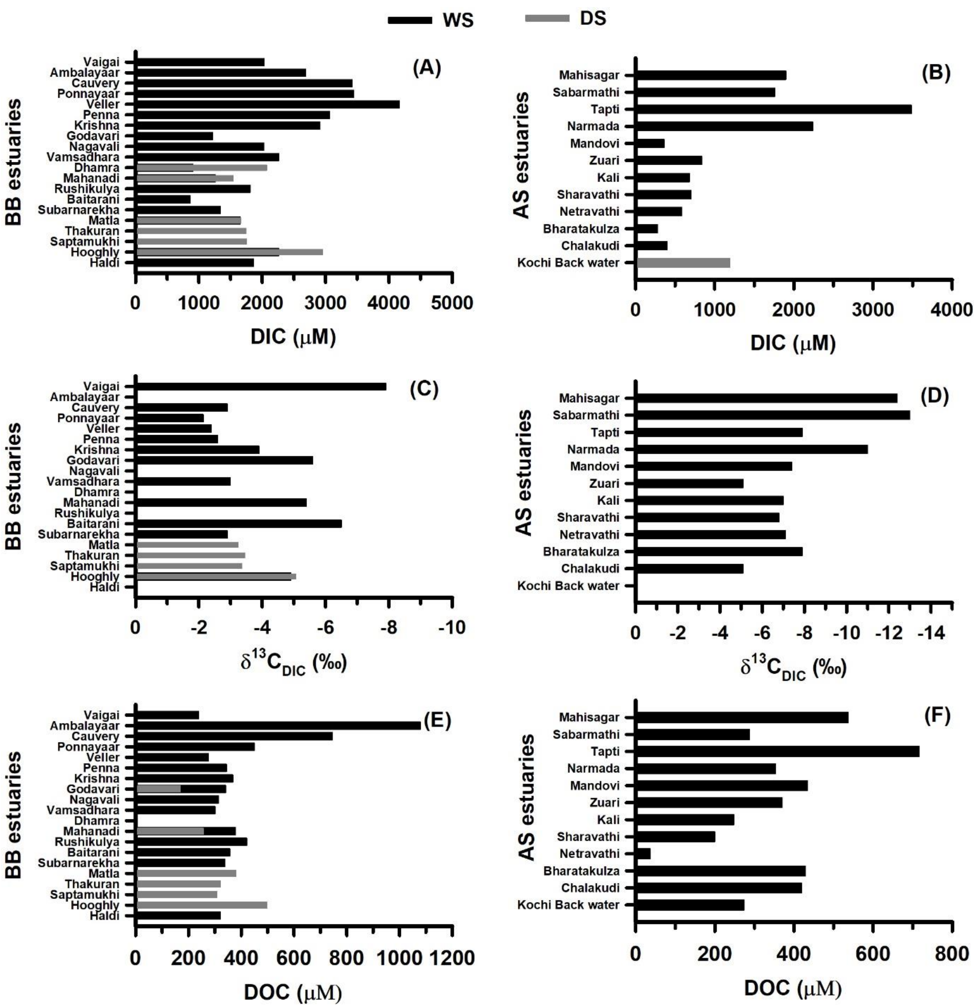

Fig.3: Variabilities of DIC, $\delta^{13}C_{DIC}$ and DOC in the major Indian estuaries. For the Hooghly, Saptamukhi, Thakuran and Matla, mean of data reported by Dutta et al. (2019a, 2021) during pre- and post-monsoon are used as dry season data. In other cases, mean data is used where multiple data is available. WS = wet season; DS = dry season.

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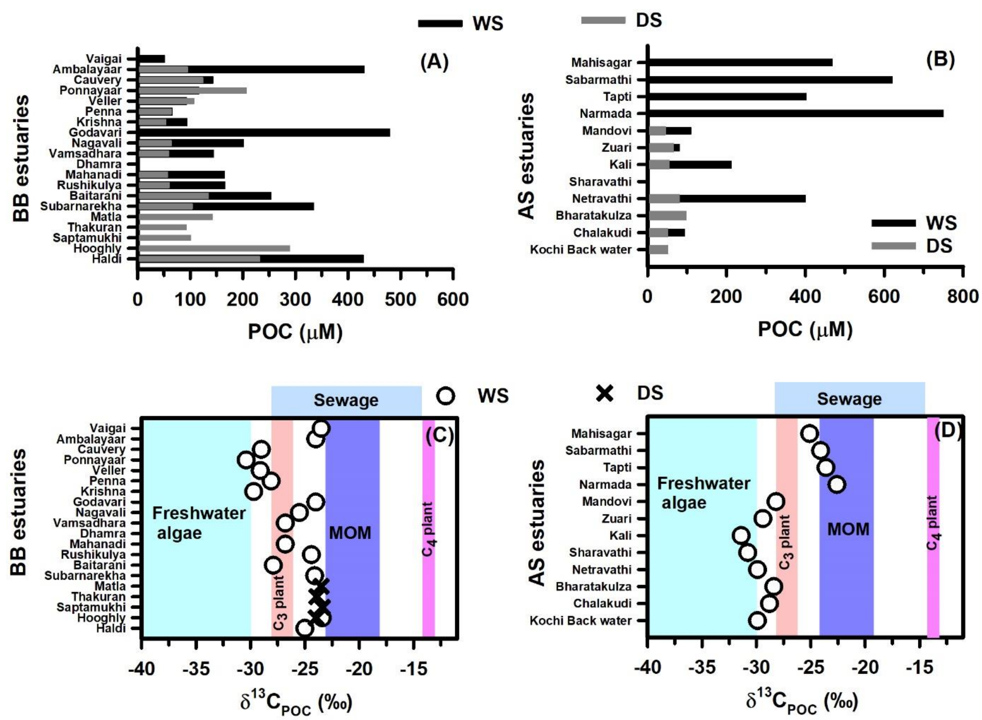

Fig.4: (A) POC distribution in the BB estuaries, (B) POC distribution in the AS estuaries, (C) $\delta^{13}C_{POC}$ in the BB estuaries, and (D) $\delta^{13}C_{POC}$ in the AS estuaries. WS = wet season; DS = dry season; MOM = marine-derived organic matter.

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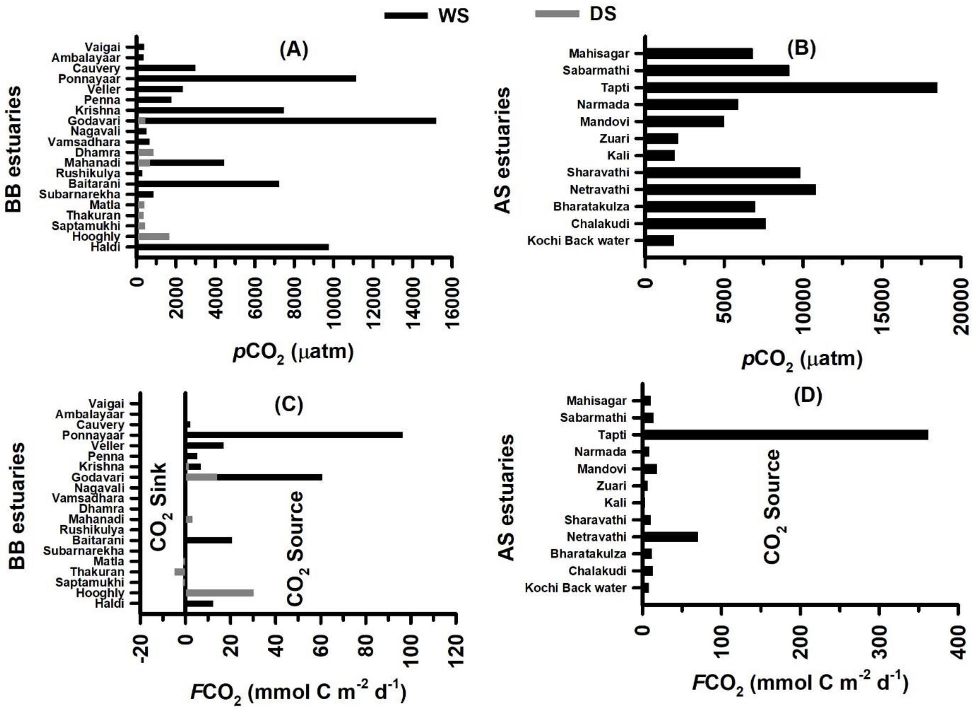

Fig.5: (A) pCO_2 in the BB estuaries, (B) pCO_2 in the AS estuaries, (C) FCO_2 in the BB estuaries, and (D) FCO_2 in the AS estuaries. WS = wet season; DS = dry season

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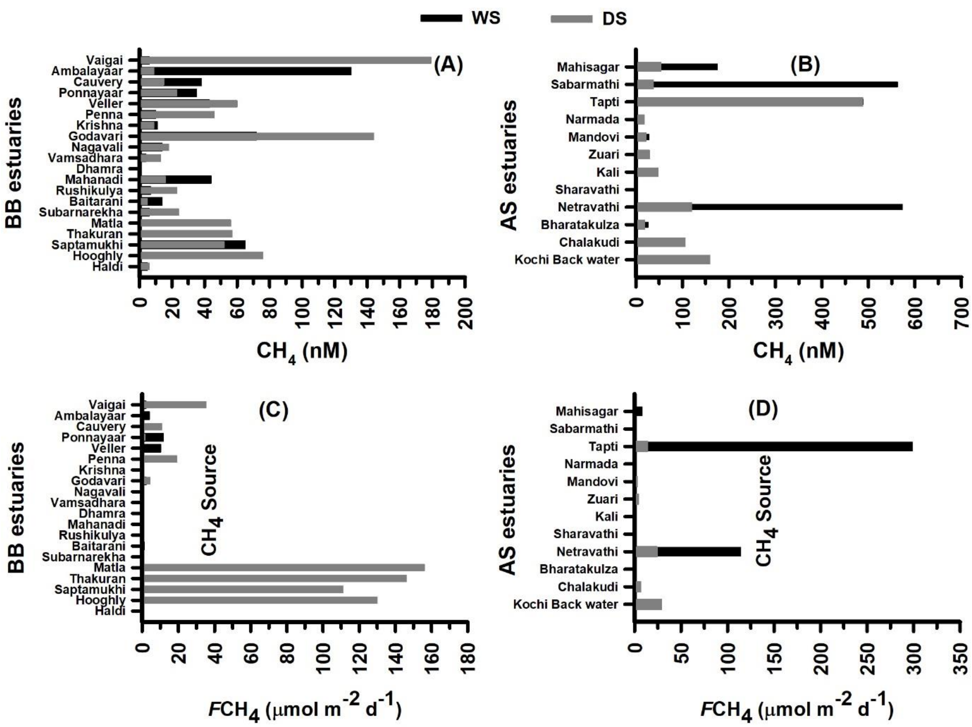

Fig. 6: (A) CH_4 in the BB estuaries, (B) CH_4 in the AS estuaries, (C) *F*CH_4 in the BB estuaries, and (D) *F*CH_4 in the AS estuaries. WS = wet season; DS = dry season

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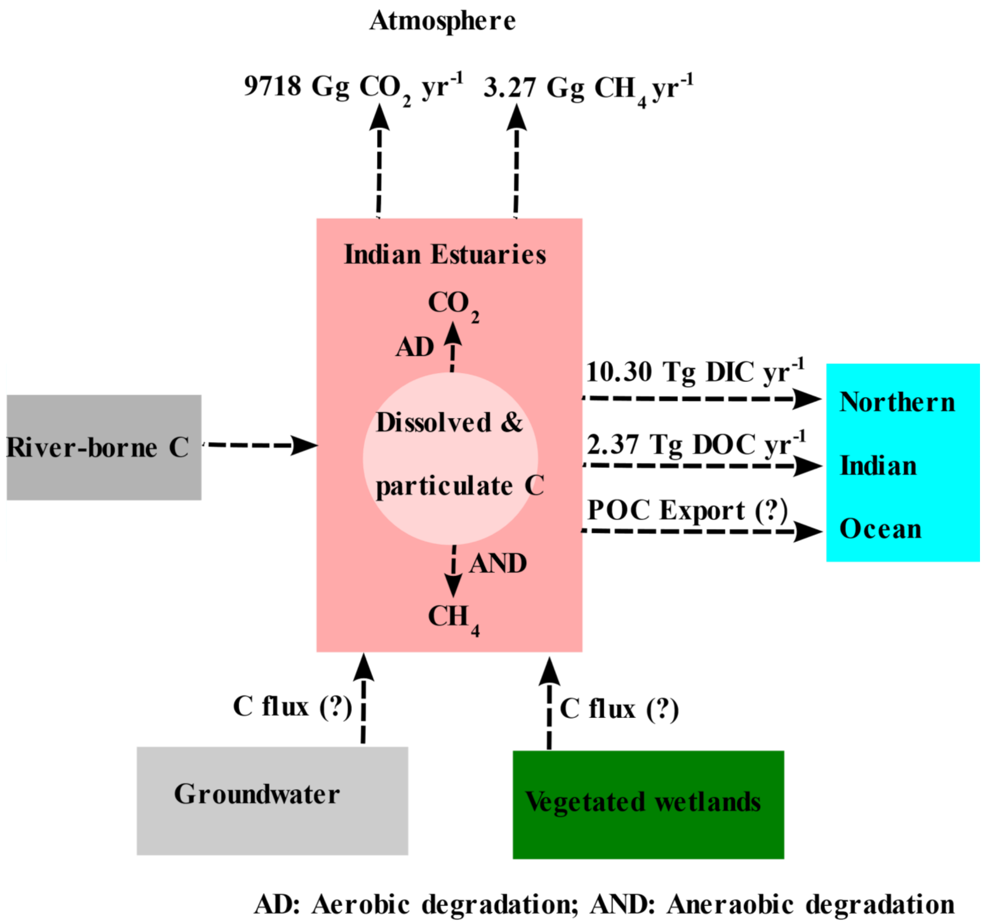

Fig. 7: A schematic diagram presenting dissolved and particulate C fluxes to/from the estuary. Magnitude is presented where available.