Biogeosciences
Discussions

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Interactive comment on "The postmonsoon carbon biogeochemistry of estuaries under different levels of anthropogenic impacts" *by* Manab Kumar Dutta et al.

Manab Kumar Dutta et al.

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Comment: Review of Dutta et al "The postmonsoon carbon biogeochemistry of estuaries under different levels of anthropogenic impact". Submitted to Biogeosciences. This study presents data from a single cruise in 2 Indian estuaries to try and decipher differences in carbon cycling between a 2 Indian estuaries with differing levels of anthropogenic influence. After reading and rereading this paper several times, it is unclear what the purpose of this study is. There is no defined hypothesis to be tested, and while the title suggests there will be some kind of comparative analysis to look at anthropogenic impact on carbon cycling (an interesting and important topic), I am left

a little underwhelmed with the analysis undertaken. The entire manuscript is based single sampling campaigns, which while not ideal is not the main issue. The main area of concern is the lack of any direction in the paper, and the somewhat descriptive and qualitative nature. I suggest that the authors define their hypothesis more clearly, and use the data to test this hypothesis.

Response: Thanks to reviewer for going through our manuscript and providing valuable suggestions which will help to improve the quality of the revised version. We understand the concern he has raised and we are trying to improve the manuscript accordingly. As we have said in the response to reviewer 1, the main objective of the present study is to bring out contrast in different components of the carbon cycle of anthropogenically affected Hooghly estuary and mangrove-dominated estuaries of the Sundarbans during postmonsoon. As suggested by the reviewer later in comments, we have introduced a table bringing out the differences in basic characteristics of these two systems, which will help the readers to appreciate the differences in anthropogenically affected and mangrove-dominated system. As suggested by the reviewer, in the revised version, given the contrasting nature of the estuaries, we also propose to bring out a central hypothesis. The central hypothesis of this study would be: exchange of CO_2 to be significantly higher in anthropogenically impacted estuary than the mangrove-dominated estuary during the postmonsoon. Given the larger spatial coverage of the mangrove-dominated estuary during the present (so far only one estuary in this system has been studied), there is a need for this hypothesis to be tested on wider spatial level.

I have a series of comments below, some minor some major that may help.

Comment: Abstract I am not convinced that the data as presented can be used to draw such strong conclusions as to the drivers of carbon dynamics in the studied estuaries. For example, Ln 35-38 The evidence supporting these processes is weak at best – no measurements of production, carbonate dissolution nor pore-water exchange were measured, and the spatial trends in concentrations and isotopes (and relationships

between carbon variables and DO etc.) were not strong enough to draw any distinct conclusions on the importance of these mechanisms. Same goes for lines 45-47.

Response: Based on the specific comments of the reviewers, we have re-analysed the data and reassessed the role of processes he is referring to in sentences mentioned above. In the response to comments below, he will find that we have either discarded the descriptive part or backed the processes active with reanalysis of the data during the present study.

Comment: Line 49 – 52. I am unconvinced that the observed trends are shown to be directly linked to anthropogenic influence. Yes, the estuaries appear to differ, but what else might be driving this. For example, looking at salinity and pCO2 in the 2 different estuaries – the highest salinity in the "anthropogenically" impacted estuary is lower than the lowest salinity in the "undisturbed" estuaries. Could the observed differences simply be related to freshwater input? What are the nutrient concentrations in the 2 estuaries? How different are they in hydrodynamics (looks like the geomorphology is distinctly different between the 2 estuary types from Fig 1). These are just a few of the alternative reasons to look at for explaining the differences observed

Response: Based on the comments from both reviewers, we have provided a table in the supplement (point - 1), which will help readers to understand the basic differences between the two estuaries. The present study was carried out during postmonsoon season, which brings significant amount of freshwater inputs to the region. Moreover, the Hooghly undergoes sever anthropogenic stress as it passes through industrial areas as well as one of the most densely populated region in India (included in table). We revisited the data in light of the comments from both reviewers and in responses we discuss the changes and processes active in the two estuaries, which led to observed difference.

Introduction

Comment: Ln 59 – 60 What is meant by "record biogeochemical and hydrological

processes"?

Response: We meant physical/hydrological processes such as mixing between marine and freshwater, tide and wave action, sediment transport etc. and biogeochemical processes such as primary productivity, organic matter decomposition etc. We believe the reviewer was concerned with 'record'. We will modify the sentence in the revised manuscript.

Comment: Ln 67 – Richey is not correct ref for this statement (Richey paper is on Amazon)

Response: Thanks to point this out. We will modify the statement with correct reference.

Comment: Ln 68 – 70 – Still large uncertainties on estuarine CO2 flux – look at error bars on Cai, 2011 estimate Response: We will point out this issue in the revised manuscript.

Comment: Ln 76 What is meant by "biogeochemical characteristic"?

Response: We meant with regards to cycling of bio-available elements, such as C, N and P. We will change this sentence to more specific.

Comment: Ln 78 – 79 Not always – see Cotovicz Jr, L. C., Knoppers, B. A., Brandini, N., Costa Santos, S. J., & Abril, G. (2015). A strong CO_2 sink enhanced by eutrophication in a tropical coastal embayment (guanabara bay, rio de janeiro, brazil). Biogeosciences, 12(20), 6125-6146. doi:10.5194/bg-12-6125-2015

Response: Thanks for this reference. In the revised version, the sentence may look like: 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 organic matter gets mineralized within the system (Servais et al., 1987; Ittekkot, 1988; Hopkinson et al., 1997; Moran et al., 1999). However, this is not always the case as observed in Guanabara Bay, Brazil, which acts as a strong

CO2 sink enhanced by eutrophication (Cotovicz Jr. et al., 2015)."

Among others

Comment: Ln 81 – 84 There has been a lot of work on mangrove carbon cycling work done since Dittmar and Larra's work in the early 2000's. Might be worth looking at more recent papers to see how far our understanding has come since then.

Response: Sure. We will modify this section in the revised manuscript. Following information may be added: Around ~50% of mangrove net primary productivity (112-160 Tg C yr-1) is imbalanced by various sinks as estimated by global mangrove C budget (Bouillon et al., 2008, Alongi, 2009, Breithaupt et al., 2012). Litter fall is identified as a primary source of mangrove derived C input in mangrove sediment and fate of this C remains a topic of research. Earlier studies reported that mangroves were responsible for ~10% of the global terrestrial derived POC (Jennerjahn and Ittekkot 2002) and DOC (Dittmar et al. 2006) export to the coastal zones. However, recent studies proposed DIC exchange as major C export pathway from mangrove forests, which is responsible for ~70% of the total mineralized C transport in coastal waters (Maher et al., 2013 Alongi, 2014; Alongi and Mukhopadhyay, 2014). Another study reported groundwater advection to be responsible for 93–99% of total DIC export and 89–92% of total DOC export to the coastal ocean (Maher et al.,2013). Upon extrapolating these C 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). After its outflux as DOC, DIC and POC from mangrove system to the adjoining aquatic system, the remaining mangrove C gets buried in sediment layers to participate in anaerobic reactions in subsurface deep sediment layers or undergoes long-term sequestration (Jennerjhan and Ittekkot 2002; Barnes et al., 2006; Kristensen and Alongi, 2006; Donato et al., 2011; Linto et al., 2014).

Comment: Ln 104- 106 Give some quantitative data to support your "anthropogenically influenced" argument. What are nutrient concentrations like? Population density? Land

use? Freshwater inflow? Etc etc. A table compiling this data would give the reader an instant understanding of the differences.

Response: Thanks to the reviewer for bringing this point. Reviewer 1 has also asked to include some information in this context from literature. Texts or a table comparing the Hooghly and Sundarbans during postmonsoon based on nutrients concentration, Chla, population density and freshwater inflow will be introduced in the revised manuscript. The information in tabular form is attached as Supplement file (point - 1).

Comment: Line 117 What is meant by positive and negative feedback here? These terms are not really applicable to biogeochemistry as a whole, but may be related to specific mechanisms/cycles.

Response: Ok. In the revised manuscript we will change this statement as follows: The postmonsoon sampling was chosen because of relatively stable estuarine condition for spatial sampling and reported peak mangrove leaf litter fall during this season (Ray et al., 2011), which may have influence on estuarine C dynamics.

Comment: Ln 137-140 Clearly there is freshwater input – the salinities are very low. In fact, my thoughts are that these freshwater inputs are a main driver of the observed differences.

Response: The freshwater input in the estuaries of Sundarbans is evident from the salinity values (12.64-16.69) during the study period. However, if you see the salinity values in the Hooghly estuary during the same season (0.04-10.37), the extent of freshwater input in Hooghly is far greater. Because of this reason, we stated 'no perennial source of freshwater and limited anthropogenic input during monsoon". We may change the sentence as: The present study was carried out in three major estuaries of the Indian Sundarbans (Saptamukhi, Thakuran and Matla) covering upper, middle and lower estuarine locations."

Comment: Ln 159 Assume the filters were GF/F filters – add these details.

Response: Yes, as reviewer stated it was Whatman GF/F filters. We will include it in the revised manuscript.

Comment: Ln 161 Accuracy of TAlk measurements. Were CRMs measured (hope so!). Also add accuracy/precision etc of all other parameters.

Response: Uncertainties were as follows: Water temperature: $\pm0.1^\circ C$, Salinity: ±0.1, DO: ±0.1 mgL-1, DIC: <1%, δ13CDIC: < $\pm0.10‰$ DOC: ±52 μgL-1, POC: <10%, δ13CPOC: < $\pm0.10‰$ pCO2: $\pm$ 1%. Yes, accuracy of TAlk was tested using Dickson standard (CRM: Batch – 131) and uncertainty was found to be $\pm1\mu$molkg-1.

Comment: Ln 196 – 198 What were the input parameters for measuring pCO2? What disassociation constants were used etc?

Response: The pCO2 was calculated using TAlk, pH, water temperature and salinity and the dissociation constants were calculated following Millero, (2013). We will include that information in the revised manuscript.

Comment: Ln 205 – 208 Why use L&M relationship? Need some kind of justification here other than saying it is conservative.

Response: Unfortunately, we don't have data on estuarine current velocity which along with wind speed is used for flux calculation as it is believed that turbulence of estuary might have an effect on air-water trace gas flux calculation. Based on only wind velocity, the L&M relationship is one of the most reliable and tested methods for flux calculations, which has been used in previous studies in the region as well (Biswas et al., 2004).

Results

Comment: Do not compare and contrast your data with previous studies in the results. Just report your data.

Response: We will remove the comparison part from the result.

Discussion

Comment: Ln 289 – 293 What are the implications for these findings? Need to dig deeper or remove.

Response: Our intension was to present influence of salinity on pH and provide the information at the beginning that this region is a bicarbonate dominated system. We will remove the sentences in the revised version.

Comment: Ln 306-311 (and Fig 3b) How was the conservative d13C-DIC mixing line calculated? Looks like you have simply added a linear relationship between the 2 endmembers, the relationship is generally not linear (See Fry, B. (2002). Conservative mixing of stable isotopes across estuarine salinity gradients: A conceptual framework for monitoring watershed influences on downstream fisheries production. Estuaries, 25(2), 264-271. Also as you do not have any mineralogy of carbonates – I would avoid using the term "calcite" precipitation, change to "carbonate" precipitation.

Response: Conservative δ13CDIC mixing line was calculated using the expression given by Mook and Tan (1991) as given in the attached supplement file (point - 2). We will change 'calcite precipitation' as 'carbonate precipitation' in the revised manuscript.

Comment: Ln 323-325 – What does DO tell you about primary production? Looks like DO is generally under-saturated?

Response: The influence of primary productivity (PP) and/or CO2 outgassing on DIC at the mixing zone was evident from mixing plot between ΔDIC and $\Delta\delta$13CDIC. We tried to go further and decouple these two processes based on TAlk - DIC relationship. However, as suggested by the reviewer, due to lack of PP measurements and level of DO indicate that it may not be a stretch. We will be remove this part from the manuscript.

Comment: Ln 335-338 Describe all the terms in this equation in the following text

Response: Here, DIC and DICCM indicate DIC concentration of the sample and DIC concentration due to conservative mixing, respectively. The δ13CDIC, δ13CDIC(CM)

and $\delta 13CMangroove$ indicate C isotopic compositions of DIC of the sample, C isotopic composition of DIC under conservative mixing, and C isotopic composition of mangroves, respectively. We will include it in the revised manuscript. Additionally, in the revised manuscript, $\delta 13CMangrove$ will be changed as - 28.4‰ as reported by Ray et al. (2015) for the Sundarbans system.

Comment: Ln 359 Where do the TAlk/DIC numbers come from? The stoichiometric relationship should be based on the slope of the line over the whole estuary, rather than individual data points – therefore not sure how you have a range here.

Response: Thanks to the reviewer for this suggestion. Based on his advice, we will make necessary changes in the text and improve this section on following lines: High pCO2 and DIC along with low pH and TAlk/DIC are general characteristics of groundwater, specially within carbonate aquifer region (Cai et al., 2003). Although all the parameters of groundwater inorganic C system (like pH, TAlk and pCO2) were not measured during the present study, groundwater DIC were ~5.57 and ~3.61 times higher compared to average surface water DIC in the Sundarbans and Hooghly, respectively. The markedly higher DIC in groundwater as well as similarity in its isotopic composition with estuarine DIC may stand as a signal for influence of groundwater on estuarine DIC, with possibly higher influence at the Sundarbans than Hooghly as evident from the slope of the TAlk - DIC relationships (Hooghly: 0.98, Sundarbans: 0.03). In the Sundarbans, to the best of our knowledge, no report exists regarding groundwater discharge. Contradictory reports exist for the Hooghly where Samanta et al. (2015) indicated groundwater contribution at low salinity regime (salinity < 10, same as our salinity range) based on 'Ca' measurement, which was not observed based on 'Ra' isotope measurement in an earlier study (Somayajulu et al., 2002).

Comment: Ln 364 – 368 Give details on this calculation. Just using the discharge rate and pore water DIC concentration I get a different value.

Response: Advective DIC flux from intertidal mangrove sediment to estuarine water

column (FISW) was computed using the relation (Reay et al., 1995); FISW = $\Phi.\nu.C$; where, Φ = porosity of sediment = 0.58 (Dutta et al., 2013), ν = average linear velocity = $d\Phi-1$ (d = specific discharge), C = DIC concentration in intertidal sediment pore water. So ultimately: FISW = d.C. During postmonsoon, d = 0.008 cm min-1 (Dutta et al., 2015a). Therefore, FISW = (0.008 cm min-1 x 13.43 mmolL-1) = 0.107mmol.cm.min-1/1000cm3= 0.000107 mmol cm-2 min-1 = 1.07 mmol m-2 min-1. In Sundarbans, tides are semidiurnal in nature, so depending upon changes in hypsometric gradient discharge of pore water will be effective during low period only (i.e. 12 hours). So, FISW =1.07 mmolm-2min-1 = (1.07 x 60 x 12 mmolm-2d-1) =770.4 mmolm-2d-1. There is a marginal difference in the manuscript, which will be corrected. We will put the formula for calculation in the revised manuscript. We hope calculation is clear to the reviewer.

Comment: Ln 383-390 – Not sure that looking at pCO2 VS DOC gives any indication as to the importance of pore-water exchange! Could also simply be freshwater input from upstream, surface water runoff, or simply leaching/respiration.

Response: We have suggested to modify the DOC section which does not include the above argument. Please see response to reviewer 1 which deals with DOC (section 4.3).

Comment: Ln 412 Give details about the "jute" industry.

Response: This is an industry based on fiber of Corchorus plants, which is used in fabrics for packaging a wide range of agricultural and industrial commodities that require bags, sacks, packs, and wrappings. Locally this is known as Jute industry. We will put the scientific name of the plant in the revised manuscript.

Comment: Ln 424-426 The POC isotopes could simply be related to the relative amount of freshwater inputs in each system (this can also be applied to most of the other differences observed)

Response: If relative amount of freshwater in each system had a major control on POC

isotopes, we would expect salinity dependent δ13CPOC variability, which was not noticed. We can modify the referred sentence on following lines: The δ13CPOC - salinity relationships in the Hooghly (freshwater region: p = 0.20, mixing region: p = 0.79) and in the Sundarbans (p = 0.65) did not confirm significant influence of freshwater on δ13CPOC. However, on an average, δ13CPOC at the Hooghly (− 24.87 ± 0.89‰ was relatively lower compared to that of Sundarbans (âĂŤ23.36 ± 0.32‰ suggesting relatively higher influence of terrestrial inputs in the Hooghly.

Comment: Ln 431-446 I am unsure why anaerobic respiration (which is energetically les favourable than aerobic respiration) would be more important in a well oxygenated estuary. The authors should expand this to explain things more clearly or remove.

Response: We will remove the anaerobic respiration part from the revised manuscript.

Comment: Ln 447-451 What is the importance/implications of this – expand or remove.

Response: The intension was to quantitatively explore dominant OC form (DOC or POC) in total OC pool and dominant dissolved C form (DIC or DOC) in total dissolved C pool in the estuary. We will remove the lines as reviewer suggested.

Comment: Ln 455 – 460 These sections seem to contradict each other. Initially it is stated mangrove inputs are insignificant – then pore-water exchange of mangrove derived CO2 is highlighted as important?

Response: For the revised manuscript, ECO2 - AOU relationship (as suggested by the reviewer) was investigated (please see response to a later comment). The significant positive relationship between the two (ECO2 = 0.057AOU + 1.22, r2 = 0.76, p = 0.005, n = 8) suggested influence of OM respiration on pCO2 in the Sundarbans. Although, the calculated slope (0.057) was markedly lower compared to the slope for Redfield respiration in HCO3- rich environment [ΔCO2: (-ΔO2) = 124/138 = 0.90, Zhai et al., 2005] indicating effect of OM mineralization in controlling pCO2 to be not so potent. Therefore, possibility of pore-water mediated CO2 influx cannot be totally neglected in

mangroves. Although based on present dataset (only low tide phase sampling) it is not possible to justify the argument, a signal for it was also observed from 24 hours pCO2 observation in the Matla estuary (Sundarbans) by Akhand et al. (2016). We will add these observations in the revised version.

Comment: Ln 463 – Cai ref – there are plenty of mangrove references for this process, might be more appropriate to use some of those here

Response: We agree. We will include some other mangrove references in the revised manuscript, such as Call et al. (2015), Bouillon et al. (2007).

Comment: Ln 463 – 466 How about plotting ECO2 vs AOU (in molar units). Look at the slope of the line. This will give a better indication of the importance or aerobic vs anaerobic R.

Response: In the Sundarbans, barring three locations (S3, T3 and M2), a positive correlation between ECO2 and AOU was noticed (ECO2 = 0.057AOU + 1.22, r2 = 0.76, p = 0.005, n = 8) suggesting aerobic OM mineralization in the system, particularly in the upper region. Although, the calculated slope (0.057) was markedly lower compared to the slope for Redfield respiration in HCO3- rich environment [ΔCO2: (-ΔO2) = 124/138 = 0.90, Zhai et al., 2005] indicating effect of OM mineralization in controlling pCO2 to be not so potent. Also, the effectiveness of salinity on pCO2 was ruled out based on pCO2-salinity relationship in the Sundarbans. No significant relationship between ECO2 and AOU was observed in either freshwater or mixing zones of the Hooghly estuary suggesting limited role of organic matter respiration on CO2. However, significant positive and negative relationships between pCO2-salinity were noticed in the freshwater (r2 = 0.71, p = 0.04) and mixing zones (r2 = 0.72, p = 0.03, n = 6) of the Hooghly. The positive pCO2-salinity relationship coupled with no significant relationship between ECO2 and AOU suggest exogenous CO2 supply in freshwater region (probability from surface runoff), whereas freshwater mediated addition of pCO2 is evident in the mixing zone. In the revised manuscript, we will explain these observations.

Comment: Ln 470 – 473 How was gas exchange and the differences between CO2 and O2 coupled into this calculation? Also how does this value compare to your air-water CO2 fluxes (you will need to normalize your volumetric rates to surface area for comparison)

Response: In both freshwater and mixing zone of the Hooghly estuary, no evidence for significant impact of aerobic OM respiration on pCO2 was found. Therefore, we will remove this section from the revised version.

Comment: Ln 480 – I think your global value for mangrove systems (63 umol/m2/d) should be 63 mmol/m2/d – which is much higher than the fluxes measured in this study.

Response: We are thankful to the reviewer for pointing this out. We have rechecked the value from Call et al. (2015). The actual value (range) is $\sim$ 43-59 mmol C m-2d-1. We will correct it in the revised manuscript.

Conclusions:

Comment: Point 1 – this variability is likely simply linked to the variability in salinity (and therefore freshwater inputs) between the studied estuaries.

Response: Freshwater inputs definitely has a role to play in the variabilities observed. However, these variabilities are also linked to in situ processes in the estuaries as described in our responses to both the reviewers.

Comment: Point 2 – Unconvinced that primary production has been shown to be the main controlling factor on DIC. Without any measurements of PP or some more thorough analysis of other potential mechanisms, this statement is far too strong

Response: We agree with the reviewer. We will modify the DIC section accordingly. As we said in our response earlier, we were trying to decouple the CO2 outgassing and PP for locations which were falling into that quadrant of ΔDIC and $\Delta\delta$13CDIC plot. However, due to lack of direct PP data, we have decided to not do that in the revised

manuscript.

Comment: Point 3 – I see no strong conclusive evidence of either of these points. Again statement is too strong without measurements of DOC flocculation or porewater exchange of DOC

Response: In light of the comments from both the reviewers on this section, we are proposing to significantly modify the DOC section. Please see our response to reviewer 1 in this regard (response for section 4.3). We have avoided emphasizing the processes for which we do not have direct data.

Comment: Point 4 Assume this is based on isotopes? Again this could simply be related to the marked differences in freshwater content within each of the estuaries.

Response: If relative amount of freshwater in each system had a major control on POC isotopes, we would expect salinity dependent δ13CPOC variability, which was not noticed. We can modify the referred sentence on following lines: The δ13CPOC - salinity relationships in the Hooghly (freshwater region: p = 0.20, mixing region: p = 0.79) and in the Sundarbans (p = 0.65) did not confirm significant influence of freshwater on δ13CPOC. However, on an average, δ13CPOC at the Hooghly (– 24.87 $\pm$ 0.89‰ was relatively lower compared to that of Sundarbans (âĂŤ23.36 $\pm$ 0.32‰ suggesting relatively higher influence of terrestrial inputs in the Hooghly.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2018-310/bg-2018-310-AC2-supplement.pdf