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Interactive comment on "Seasonal variability of the inorganic carbon system in a large coastal plain estuary" *by* Andrew Joesoef et al.

Anonymous Referee #2

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General comments

This manuscript deals with the seasonal variability of the carbonate system in the Delaware estuary, a large estuary along the eastern U.S. coast, and focuses specifically at quantifying the role of riverine DIC and TA inputs therein. It presents high-quality data obtained by the authors in both the estuary and rivers, as well as daily discharge and long-term riverine monitoring data from USGS. I overall enjoyed reading the manuscript and consider it robust, but I don't find its main conclusions very remarkable and was somehow left with the feeling that more could be done with the available data.

The authors mention studying the DIC:TA ratio as a relative novelty in this manuscript (I find the term "rarely studied" as used in the abstract a bit strong) and I agree that this should deserve more attention in the literature in the context of minimum buffering capacity at the point where DIC≈TA. However, when presenting these data and trying to put so much focus on them, I expected the authors to do some more quantitative work on this, e.g. how the position of the DIC=TA point in the estuary varied over the course of the year and what role the riverine input played therein. This would, in my opinion, increase the impact of this work.

The manuscript seems to be written by multiple authors coming from different background (freshwater versus marine communities). This leads to overall imbalances in the manuscript, with certain topics being discussed much more extensively, and also more quantitatively, than others. Specific examples are given below. The authors should generally try to better unite the several parts of the manuscript.

Specific comments

I found the introduction particularly unbalanced. Specifically, I think that the first paragraph of the introduction (p. 2, l. 7-24) can be shortened, whereas the second and third sections may be extended. As the main research area is an estuary, I'd expect discussions of carbon cycling on both the freshwater and marine sides, whereas here, only the freshwater side is discussed. I also miss a description of how waters from both sides interact and mix in the estuary, i.e. a section on (seasonality in) C cycling in estuaries.

The authors do not clearly explain in the manuscript why increases in both DIC and TA indicate inputs of HCO3-, whereas an increase in DIC only must mean an input of CO2. This may not be common knowledge to everyone and should be mentioned in the introduction.

p.6, l.29 - p.7, l.1: I miss some methodological details here. In case surveys were longer than 1 day, was the average discharge for the whole cruise period taken? (this also applies to l.18-20). Plus, I understand that on an annual scale it is valid to assume that discharge at the seawater endmember is the same as riverine discharge, but is this

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Discussion paper

valid at the time scale of separate surveys (as presented in Table 3) as well? There is another point in the manuscript where these different temporal scales come into play and that is in the context of calculating NEP in section 4.5. If I'm not mistaken, here annual averages for the import and export fluxes are used, whereas it is convincingly shown for at least the import fluxes that there is considerable temporal variability. If the authors did take this into account in their calculations for Fig.9, they should write this more clearly. If they didn't take this into account, I have my doubts about the calculated NEP values.

Section 4.1: Please discuss the reliability and quality of the long-term monitoring data. Such data are often known to display unrealistic trends due to e.g. methodological changes. Also, I do not believe that Fig. 6b displays a real trend as the y-axis variable highly depends on the x-axis variable (as is also shown in Fig. 6d).

Section 4.2, p.9, l-10-13: Don't the authors have enough data available to make a simple linear mixing model at the point where the Schuylkill and Delaware rivers meet near Philadelphia, to actually test and quantify the hypothesis postulated here?

Section 4.3: The authors discuss long-term trends in alkalinity, but as riverine TA export is the product of concentration and discharge, it would be interesting to discuss long-term trends in discharge patterns as well. With the high-resolution data available, the authors can focus not only on long-term trends in discharge, but also on changes in the numbers and intensity of episodic events. Also, the authors disregard the fact that these historical riverine TA data have been previously published and discussed (Kaushal et al., 2013). They should at least refer to this work, and I feel that this manuscript can benefit from the (quantitative) way that work explored possible drivers for the long-term trends. In what has been discussed by the authors, I miss a discussion of the role of increased temperature, which can enhance weathering but has not been shown to the primary driver of weathering in the Baltic Sea catchment (Sun et al., 2017).

p.11, l.12-17: It could be me but this sentence reads like: "Because of X, we assume

X". But, more importantly, the authors do not discuss the validity of their assumption of upscale not only the discharge but also the import fluxes. How valid is it to assume that the remaining 30% of discharge has DIC and TA concentrations equal to the weighted average of the three major rivers?

p.12, l.3: "small riverine systems" No, as these have already been taken into account by upscaling the riverine discharge. I would also suggest to specify groundwater discharge as an additional source here, rather than pooling it into the various external sources.

Section 4.5: I feel that the estimate of NEP can be discussed a bit more in the context of previous work in the estuary. For example, earlier measurements of production and respiration in the estuary also pointed at the latter exceeding the former (Preen and Kirchman, 2004). I am sure there is more relevant work done, perhaps also on the role of salt marshes and groundwater discharge in this system. Also, on p.12, l.27 marshes are mentioned as a possible source of CO2 into the bay, whereas on p.10, l.24-29 it is discussed that the export of DIC from salt marshes is small. So can they really be a substantial CO2 source?

Conclusions: p.13, l. 28-30: The manuscript does not quantify how important seasonal changes in NEP are relative to variations in river discharge and mixing on the same time scale. This ties in with one of my earlier comments on time scales, but would it be possible to show how the relative contribution of NEP versus river discharge changes over the course of the year?

Technical corrections

p.1, l.17: define HCO3- before using it.

p.1, l.19: same here for CO2

p.1, l.19-21: this sentence is not very clear. I would at least suggest writing "additional DIC input in the form of CO2" instead of "additional CO2 input", and perhaps do some more rephrasing.

p.1, l.27: “CO2 flux” should be termed “net DIC production” or, as used later in the manuscript, “net ecosystem production”.

p.1, l.27: replace “inclusive of” with “including”

p.1, l.27 - p.2, l.3: It is the small difference between riverine input and export that suggests that most of the DIC produced in situ is lost within the atmosphere, not the fact that in situ production is small to the riverine input. Please rephrase this.

p.2, l.22: add in which form the DIC is transported here (HCO3 or CO2) and whether this depends on silicate versus carbonate weathering.

p.2, l.25: supply of DIC by rivers. . . add “to estuaries”

p.4, l.8-11: add a short description of the general circulation pattern

p.4, l.13: I miss some basic information here: how many stations were measured each cruise, and what were the coordinates of these stations? The trajectory and stations can easily (and should) be added to Fig. 1.

p.4, l.20: Add a reference to Fig.1 here

p.4, l.22: Add a reference to Fig.2 at the end of the sentence.

p.4, l.28: “preserved at”. Also, how long were the samples stored before analysis?

p.5, l.7: What are the accuracy & precision of the pH measurements? What is the potential error with the NBS scale in the more saline waters?

(related to the previous question) p.5, l.18: Here, pH is suddenly mentioned with 3 significant digits, whereas in l.15 and Table 1 only 2 significant digits are given. Please be careful and consistent here.

p.5, l.20: A comma is used here as thousand separator, which is not done in other parts of the manuscript. Please be consistent here.

p.5, l.28-30: I feel this is part of the discussion.

p.6, l.4-6: What do the authors exactly mean with “TA” in l.5? The average concentration of riverine TA? Please clarify.

p.6, l.23: “varied linearly. . .” add “with salinity”

p.7, l.29: not only respiration from soil OM, but also imbalances between production and respiration along the aquatic continuum can impact DIC:TA ratios.

p.9, l.19: This section should be termed “Historical trends in riverine alkalinity”, not “estuarine alkalinity”

p.10, l.9-11: These deviations from conservative mixing for a specific month are really difficult to see in Fig.3.

p.11, l.6 ff.: I’d say that this is a DIC mass balance, not a CO2 mass balance. Please change this throughout the manuscript.

Table 1: Add that pH is at 25 degrees and on the NBS scale. Also, add the in situ temperature such that the reader can get an idea of seasonality in temperature and pH at in situ temperature.

Figure 1: do the arrows point at the exact sampling locations of the rivers? It would be clearer to add symbols indicating the exact locations in the plot. Also, as said before, I miss an indication of the trajectory and/or the exact sampling locations within the estuary in this plot. What is the C&D canal?

Figure 2: add in the caption what the diamond symbols and green lines indicate.

Figure 5: I find it confusing that this plot should be read in the reverse direction as Fig.3 and suggest that the x-axis be reverted.

Figure 6: as discussed above, I suggest removing Fig. 6b (and merge 6d with 6c), as I don’t believe it to display a real trend. In the figure caption, change “data measured in

our lab” to “our data”. I would also suggest using “our data” in the legends of Figs. 6 and 7, rather than the corresponding author’s last name.

References

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