

Review #2.1

2nd Review of paper "Influences of manganese cycling on alkalinity in the redox stratified water column of Chesapeake Bay" by Aubin Thibault de Chanvalon, George W. Luther, Emily R. Estes, Jennifer Necker, Bradley M. Tebo, Jianzhong Su, Wei-Jun Cai

The paper has evolved in a positive way since the previous version: better Figures, fair explanation of the error treatment on DICex and TAex, improvement on the "negative" biogeochemical pathways. But they fail to properly answer the other points that I raised (see below my previous comments):

- The relation with the sediment is still not properly documented (any older study at that site or nearby?) but, at least, the point is tackled in the abstract and a paragraph is written to explain this link. The authors should provide literature data concerning the sediment processes.

We added the reference of Aller 2014 (Sedimentary Diagenesis, Depositional Environments, and Benthic Fluxes, in: Treatise on Geochemistry (Second Edition)) for generalities about sedimentary diagenesis reactions. Previous studies of Sholkovitz et al, 1992 and Lenstra et al., 2021 are quoted for local specificities near or the same station.

- The general statements: I recommended on my first review to shorten part 2.3.1. It was changed and some textbook part including the bow and spear section and Figures were removed. But I still find this part unnecessary long and I am convinced that it could be shortened or part of it diverted in an annex.

We follow the reviewer comment by diverted most of the equation in an Annex

- Furthermore, I had troubles during my reading with part 2.3.2. I find the definition adopted for TA (the sum of all charges that each species would have at pH=4.5) not obvious and certainly less useful than identifying bases in solution at the in situ pH and defining which processes consume or produce them. I find this part 2.3.2 not necessary, not well-named ("TA changes indicated by reaction stoichiometry"), and not clear enough to add value to the paper. I would advice to remove it.

The charge approach used to calculate TA, has been developed in previous papers (e.g. Soetaert et al. 2007) to infer the TA changes produced by a reaction that modifies simultaneously the amount of bases in solution and the in situ pH. In case of such a reaction (for example carbonate dissolution) it is not possible to identify rapidly the changes of pH (most of the DIC from carbonate dissolution is going to be HCO_3^- , but a small amount will be CO_2 and get volatilised, increasing the pH while another amount is going to form CO_3^{2-} and will decrease the pH making the direct calculation of TA very uncomfortable). In contrast, the charge approach indicate that the change of TA will be 2 (for Ca^{2+} , DIC does not contribute as it is H_2CO_3 -no charges- at pH 4.5). We modify the title and the first sentence of this section to trigger the importance of the charge transfer approach (l.174-175):

"The simplest way to calculate the TA changes induced by an individual reaction is to look at charge transfer induced by the stoichiometry of the given reaction."

- Last point: the possibility of primary production in turbid waters especially during the flood. The authors did not answer to that specific question nor provide data proving that the water was clear enough to allow primary production.

Unfortunately, we did not measure the concentration of suspended particles.

However, we quote Cerco et al, 2013 (l.424); that reports observed values always below 50 mg L⁻¹ at our station, and modelled a median below 10 mg L⁻¹ even at high runoff.

I think that the paper is heading in the right direction and that the authors should consider the comments above before being published.

Detailed comments (some):

- title: "Influences" should be replaced by "Influence" We change the title accordingly
- line 134 and after: equation numbering is missing, please check!

Equation that are not quoted in the main text were not numbered

- line 165: "spread all over the water column". Add "and also in local sediments" As described in the lines 150-158, the "zones" (we renamed it "stratum") does not include the sediment, but include local endmembers that could have been produced in the sediment before their migration upward (and before the steady state achievement).

- paragraph 3.2: too many numbers in text, add a Table with all these numbers All these numbers are extracted from the Figure 3, therefore adding a Table seems unnecessary.

- line 314: provide information on water turbidity to ensure primary production conditions were present at that time (2018)

We change the sentence into (l.312-315):

This original signature can be modelled by the combination of simultaneous carbonate dissolution (CD), the water column being undersaturated, and PP, no important turbidity was visible as modelled by Cerco et al. (2013), in equal proportion (2nd line in Table 2)

- line 380: "Figure 4c demonstrates..." I think it is rather Table 2. Please change! It corresponds to a graphical demonstration since a combination of any arrow in Figure 4c with the arrow corresponding to MnR-MnC can produce the slope of $\Delta TA_{ex}/\Delta DIC_{ex} = 2.4$.

Review #2.2

This is the third time I am reviewing the manuscript and I have thus focused on the parts of the manuscript I was most critical about in the previous rounds of review: introduction, section 2.3.1 and discussion, especially the final part. In my view, the introduction has sufficiently improved but the authors still have some work to do on the discussion and especially section 2.3.1.

General comments

The introduction has surely improved compared to the last version. There is now a link between anoxia and the carbonate system, but the unknowns and objective of this study could still be better introduced. Why is it necessary to better constrain the carbonate cycle in temperate microtidal estuaries?

We added a sentence summarizing the issues and limiting knowledge at the beginning of the last section of the introduction (l.53-56) :

“While TA controls the CO₂ buffering capacity of the ocean, riverine input of carbonate to the ocean is poorly constrained (Middelburg et al., 2020) and only rare publications take into account the estuarine transformations of the carbonate species (e.g. Su et al., 2020a; Abril et al., 2003) furthermore in a context of oxygen depletion (e.g. Abril et al., 2004). To better constrain the carbonate cycle in oxygen depleted estuaries, ...”

Section 2.3.1 has been shortened quite a bit (which is a good thing, from my point of view, as the old Figure 1 was probably redundant) and it is good that the meaning of C and D is now explicitly explained. However, the shortening comes at the expense of the readability of the first section. Eq. (1-5) include a lot of terms that are not introduced (such as alpha / stoichiometry and k / rate constant (I assume)) and I wonder how much is really necessary for the manuscript. In the end, the authors would like to show how TA_{ex} and DIC_{ex} can be used in combination with reaction stoichiometries to infer which processes can explain the observed TA_{ex} and DIC_{ex} combination (L.163-166). This means that Eq. (5) and Eq. (7) are the two key equations. I would suggest to either explain L. 118-140 more clearly (and thus expand a bit) or to keep only the essential information in (my preferred option).

We reduced the section 2.3.1 by 6 equations by diverted the most technical parts in annexes.

Maybe the text in L. 283-289 can be rewritten to include in the method section, because this text is non-technical and clearly outlines the assumptions (and confirms that Eq. (5) and (7) are indeed key).

The assumption are now outlines on l. 120-121 and in lines 159-163.

In case of turbulent diffusion mixing (sometimes called eddy diffusion) in only one direction (no lateral input), at steady state, on a portion of space where occurs one chemical reaction, the changes of concentration, C and D, of two species can be described by equation (1) (see Appendix 1 for more details):

Therefore, in a system defined between only two endmembers, away from atmospheric exchanges, in case of turbulent diffusion mixing, at steady-state and with negligible lateral mixing, the “reaction driven” approximation allows us to

interpret linear variations of ΔTA_{ex} versus ΔDIC_{ex} as a sum of biogeochemical reactions spread all over the water column that can be broken into several reactional stratum. In each stratum, if the local $\Delta TA_{ex}/\Delta DIC_{ex}$ ratio is constant, it corresponds to the apparent stoichiometry of a combination of the biogeochemical reactions occurring in this stratum.

In the previous version, both the other reviewer and I commented on the fact that it is nowhere made explicit that the reactions in Table 1 take place in the sediments and that sedimentary inputs are thus key. The abstract has now properly been rewritten to include that some of the main reactions take place in the sediment, but this needs to be clearer in section 2.3.1 as well. The authors, in their response to reviewer 1, claim that L.157-162 covers this point, but because this text is so technical this key point doesn't come out strongly at all.

We apologise our difficulty to clearly describe the concepts and thanks the reviewer for his/her remarks since it helps us to clarify the condition of application of the reaction driven approximation. We write again the lines 150-158 to better explain the implication of the local endmember definition;

However, in a stratified water column, not only one but several successive reactions occur, limiting the validity of equation (1) to each reactional stratum. The general case is not straightforward to solve, but in the particular case where the C versus D plot represents a straight line between two endmembers with different concentrations, the previous analyse of equation (2) indicates (second case) that one endmember would have been previously generated from the second by a chemical reaction with similar stoichiometry. Thus, the depths corresponding to the straight line define a reactional stratum characterised by a constant α_C/α_D and delimited by two local endmembers maintained in steady state by chemical reactions with similar stoichiometry than the one that produced them, i.e. $\Delta C/\Delta D = \alpha_C/\alpha_D$. The local endmembers should have been produced before the steady state achievement, by a reaction of similar stoichiometry but the reaction could have been faster than the observed one or could have occurred in a different place, including in the sediment.

Moreover, L.165 still mentions "spread all over the water column" which is fundamentally incorrect because the "zones" include the sediments. There are more examples of this (e.g. L.278, "in situ"). In short, the authors have to clearly define that the "reaction driven" approximation includes reactions in water column and sediment from the start.

As described in the lines 150-158, the "zones" (we renamed it "stratum") does not include the sediment, but include local endmembers that could have been produced in the sediment before their migration upward (and before the steady state achievement).

This discussion benefits from always comparing ΔDIC_{ex} with ΔTA_{ex} and ΔAOU or ΔH_2S . I agree with the majority of changes done in the discussion and also in the final part. However, I do think that the main points of section 4.5 regarding the role of sediments (L. 444-452) need to be moved to / integrated in the method section because (again) the role of the sediments in the approach has to be clear from the start.

The new version of the lines 150-158 takes into account most of the concept initially written only in the lines 444-452, in particular:

The local endmembers should have been produced before the steady state achievement, by a reaction of similar stoichiometry but the reaction could have been faster than the observed one or could have occurred in a different place, including in the sediment.

Detailed comments per line

L. 22: "carbonate signature" --> I suggest to change to "DIC/TA ratio" because this is what you refer to.

We refer to $\Delta TA_{ex}/\Delta DIC_{ex}$ ratio. It seems important to not confound TA/DIC with $\Delta TA_{ex}/\Delta DIC_{ex}$.

L. 24: "especially in river-dominated environments" --> this now reads as if it applies to all river-dominated environments, but you write yourself that the Chesapeake Bay is quite peculiar (see L. 396). Better rephrase: "the critical role of Mn in alkalinity dynamics in the Chesapeake Bay and potentially other river-dominated environments"

We changed the text according to the recommendation

L. 32: "This disequilibrium" --> which one? The DIC increase without concurrent TA increase mentioned two lines earlier? Specify.

We change by "This cationic deficiency"

L. 36: "accounts for 2/3 of buried carbonate" --> where? Shallow waters globally? Please specify. We change the sentence into (l.35-38):

However, in shallow waters, that accounts for 2/3 of global buried carbonate (Smith and Mackenzie, 2016), carbonate precipitation largely predominates over dissolution and other localised processes may constrain carbonate dynamics (Borges et al., 2006; Lohrenz et al., 2010).

L. 41: Do you mean to say that humans migrate to coastal areas because of global warming, or that global warming contributes to eutrophication? We change the sentence into (l. 43):

The global trends of human migration towards littoral areas and global warming favour eutrophication and a decrease in oxygen levels in coastal water

L. 46: "multiplies the possibilities for" --> strange formulation, what about "enhanced the possible build-up of" Thanks for the proposition, we change the sentence accordingly

L. 49 "negatively charge SO_4^{2-} " --> do you need to mention the charge now since you have removed it from the introduction? We suppressed the reference to the charges.

L. 53: "TA and DIC concentrations" I wonder here if the TA and DIC concentrations or the fluxes matter. S burial (taking place in the sediment) leads to specific pore water TA and DIC concentrations which impact water-column TA and DIC (the subject of this study) via effluxes. We agree with the proposition and change "concentrations" by "effluxes" since it better prepare the reader to the final story of the study.

L. 165: "spread all over the water column" --> and the sediments. See general comment above. We maintain our formulation since we only interpret signals from the water column. Even if the local endmember has been produced in the sediment, the reaction has still to occur in the water column to maintain the local endmember at the steady state.

L. 277: "in-situ processes" --> as opposed to mixing, but including the sediments. Again, that should be made clear here. See above, the reaction has to occur in situ also to maintain the steady state. If not, the $\Delta DIC/\Delta TA$ would not be a straight line.

L. 289-291: I am not sure if I find this a clear comparison, and perhaps even misleading as water is also moving in the opposite direction. **As proposed, we removed the comparison**

L. 294-295: "an excess of ΔTA_{ex} " --> this becomes confusing. What about: "even higher ΔTA_{ex} "? **We changed the sentence according to the comment**

L. 308: "the weakness of nitrification" --> rephrase to something like: "the relatively slow nitrification" **We changed the sentence according to the comment**

L. 321: "significant nitrification". How much approximately / at least? **We realized the sign of nitrification should be negative, therefore we changed the sentence into (l. 316-318)**

Note that the ratio between $\Delta TA_{ex}/\Delta AOU$ implicates an important nitrate assimilation superior or equal to the amount of N required for the PP, as modeled by negative nitrification in Table 2.

L. 364-365: these low concentrations may have been found in the water column, but not in the sediments where you propose that the reactions take place. So can you use it as a reason here? **Yes : the Mn^{2+} or Fe^{2+} produced in the sediment have been probably oxidized during the dephasing as the local endmember moved up into the water column. So the fingerprint on TA/DIC include this precipitation of Mn^{2+} and Fe^{2+} and have to be interpreted with solids as product of reaction.**

L. 386: "at this site" --> in the sediment or water column? **We replace by in this water column**

L. 390-392: This is quite an assumption without any sediment measurements, although I agree that on a 10-day period is it likely met.

L. 396: This line exactly indicates why the final sentence of the abstract needs rewriting.

L. 416: Title needs to be changed because global budget is removed. **We changed the title into Local budget**

Technical comments (I have not listed all)

We thanks the reviewer for all these improvements and changed the text accordingly

L. 21: "Stoichiometric changes"

L. 23-24: "as summer begins" --> "at the onset of summer"

L. 32: "to DIC"--> "with DIC"

L. 35: "a process named chemical carbonate compensation"

L. 50: "coastal waters"

L. 252: "in terms of"

Figure 4: panel (d) is not explained here.

L. 335: "significant"

L. 336: "no...were not performed" --> remove "not"