



EGUsphere, referee comment RC1  
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## **Comment on egusphere-2022-428**

Anonymous Referee #1

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Referee comment on "Influence of manganese cycling on alkalinity in the redox stratified water column of Chesapeake Bay" by Aubin Thibault de Chanvalon et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-428-RC1>, 2022

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Review of Thibault de Chanvalon et al. EGU sphere

This paper presents an original dataset of the carbonate system and major redox species in the water column of a stratified estuary with anoxic deep waters. The objective is to determine the main reactions that lead to a net production of alkalinity in the estuarine bottom waters. Based on an analysis of TA/DIC ratio and the stoichiometry of reactions, the authors conclude that MnO<sub>2</sub> reduction followed by Mn carbonate precipitation are the two main reaction that can explain the observed trends in TA. I found many problems in this MS, including several small mistakes on the principles of the carbonate chemistry in the text, figures of poor quality not appropriate to describe the processes that are discussed in the text, a presentation aggregating results and discussion that makes the authors reasoning very hard to follow, and finally, a conclusion that appears speculative and not fully supported by the data. I had hard work reading the MS because of language problems and too many shortcuts all along, but I first thought it could be reconsidered after major revision because of the high quality of the data. However, when reaching the end of the discussion, I found the conclusions speculative and not fully based on appropriate quantitative statements, so I believe the analysis should be started over and the paper in its present form could be simply rejected, or at least revised in depth.

Main problems:

1-presentation

Presentation of the results is confusing and the MS structure with a "result and discussion" section makes it worth. Choice is made to present only plots of concentrations versus salinity aggregating two sampling periods. Readers cannot get a precise idea of the vertical structure of the water column in the estuary. Conceptually, longitudinal gradients are mixed with vertical gradients without any consideration about respective mixing times. A long and unnecessary discussion is made about the choice of the freshwater end-member values (which is not a real freshwater), although it appears that most of the salinity gradient studied here occurs vertically. We have no map of the estuary with sampling points. No info about timescales, mixing of end members is analysed with little information about the timescale for the mixing to occur.

I was disappointed by the absence of real vertical profiles (some are in Fig A2, but not DIC and TA, pCO<sub>2</sub>, Sal, T, pH...) in the main text, although I understand the usefulness of the time composite salinity plot in Fig. 1 for the modelling and mass-balance purpose (assuming that the authors are able to demonstrate that the hypothesis behind such plot are valid)

2- scientific content

see mistakes and imprecisions, in line by line comments

Stoichiometric model in fig.3 does not include the possibility for gas exchange to alter DIC and AOU, at least near the surface layer. Depending on pCO<sub>2</sub> and O<sub>2</sub> %sat values at the surface, gas exchange can alter the AOU/EDIC ratio away from 1. Deviation of the O<sub>2</sub> / CO<sub>2</sub> correlation can be due to carbonate buffering effect on CO<sub>2</sub> but not on O<sub>2</sub> (see e.g. in rivers: Stets et al. (2017), doi:10.1002/2016GB005578.).

In fact, because the salinity and redox gradients are vertical at the study site, there is no need to always consider the gas exchange and its impact on DIC. Using the pCO<sub>2</sub> value at the surface, it would be possible to calculate the change in DIC due to invasion of atmospheric CO<sub>2</sub> in the first meters of the water column during the representative mixing time, and show that this change is negligible.

The main problem I see concerns the conclusion that Mn oxide reduction coupled to Mn carbonate precipitation is the "key" mechanism.

First it is not clear in the MS what are the respective roles of Mn and Fe, both appear in the title and abstract, but only Mn is considered in the stoichiometric approach. Second, the argumentation on the predominance of Mn reactions on the production of alkalinity is based only on the TA/DIC slope of 2.4 observed between the suboxic zone and the sulfidic

zone (Fig. 3). However, there are many processes and reactions potentially occurring in this transition zone and the slope of the TA/DIC ratio does not only depend on the nature of the reactions as the authors analyse, but also on the intensity of the reactions and on the mixing intensity by turbulence and vertical transport between the two layers. Indeed, at the top of this suboxic-sulfidic gradient some TA consuming processes by secondary reaction not involving organic matter can occur. So the presented analysis considering the TA/DIC slope variations with the stoichiometry of primary reactions followed by secondary reaction such as CaMn precipitation does not account for secondary reactions that may decrease the TA without changing the DIC.

Finally, the MS itself reveals the weakness of the conclusion about the importance of Mn reactions: L310 "Based on an average concentration of 20  $\mu\text{mol g}^{-1}$  of Mn in suspended particles, the 88  $\mu\text{M}$  of  $\text{MnO}_2$  would require a suspended material concentration of about 4.4  $\text{g L}^{-1}$ , which is again one or two orders of magnitude higher than the 0.01 – 0.1  $\text{g L}^{-1}$  usually found in the Chesapeake Bay."

Line by line comments

Abstract

« burial of carbonate which modulates the ability of the ocean to trap anthropogenic  $\text{CO}_2$ . ». Not clear if you refer to build up of alkalinity in the ocean, which is indeed a sink of atmospheric  $\text{CO}_2$  or burial of  $\text{CaCO}_3$  which leads to degassing of  $\text{CO}_2$  (Buffer factor 0.7, See works by Frankignoulle and Gattuso end of 90s in coral reefs). burial of carbonate would not trap anthropogenic  $\text{CO}_2$ .

L15: according to the profiles, how was NEP distributed? Positive at the surface and negative below?

You mention carbonate dissolution, but no precipitation occurs for instance in blooms at the surface?

L28 "weathering" rather than "erosion"

"enrichment not associated with a  $\text{Ca}^{2+}$  enrichment, in contrast to the  $\text{HCO}_3^-$  released from continental erosion (preponderant at thousands to a million year scale, Urey, 1952)."

HCO<sub>3</sub><sup>-</sup> also comes from dissolution of continental rocks others than carbonate rocks (100% atmospheric CO<sub>2</sub>), and thus without Ca<sup>2+</sup> enrichment.

L40 "with a high vertical resolution (down to 10 cm)." a pity we cannot see these high-resolution profiles in the MS, at least some XXX

Introduction is focussed on CaCO<sub>3</sub>, but the paper is mostly based on an analysis of TA/DIC ratios. Better introducing the principles of TA/DIC ratio analysis would be helpful

L49: eleven or "a dozen"?

L62 define DI

L93 "an excel sheet implemented with values from (Millero, 1995)" > which carbonate and bicarbonate dissociation constants and solubility coefficient of CO<sub>2</sub> ?

L100 "TA and DIC are conservative during mixing" for DIC, this is true only if no gas exchange occurs, which is the case vertically in a water column, below a certain water depth that could be calculated with the data and a simple gas exchange parameterization

L108 "Such changes were not necessary for DIC<sub>ex</sub> calculation." Why? The choice of the freshwater TA & DIC end-members looks arbitrary. Please better explain. In theory, the sensitivity of calculated DIC<sub>ex</sub> and TA<sub>ex</sub> to the values in the freshwater end-members can be calculated

L111 "the uncertainty of our description" Awkward formulation

L151 "While direct plots against depth generate noisy profiles that are less informative, plots against salinity provide consistent information about the processes.". In a section called "water column stratification", one would expect to see at minima T and S profiles versus depth. Why "noisy profiles"? are they altered by the sampling procedure? How can profiles be noisy versus depth but not versus salinity? Are salinity profiles "noisy"? Does the sampling keep the stratification intact? Is the noise due to heterogeneity induced by tidal currents despite samples being taken at tidal slack?

L152 > "River" flow

L158 "Below, with increasing depth, an important increase of pCO<sub>2</sub> accompanying the decrease of O<sub>2</sub>, pH and temperature is visible." In fact, readers cannot see anything "visible" "with increasing depth", only Fig A2 reports vertical profiles, and no S, T, pH, O<sub>2</sub>, pCO<sub>2</sub> are shown. In addition, it looks that some 2017 profiles start only at 8m, why? In Fig. 1 the surface "PP" layer is referenced as 2 meters depth, does this mean that the surface layer sampling includes only some of the stations? Why such strategy? Why no systematic surface sampling? This needs clarification

L159: "A relatively invariable low O<sub>2</sub> zone (called ILO in Fig. 1) is here defined by the depth invariance of O<sub>2</sub> concentrations, and 160 corresponds to a concentration of about 30 μM in 2017 and 110 μM in 2018. Other species are also relatively stable for this depth such as pCO<sub>2</sub>, at about 2500 μatm in 2017 and 1800 μatm in 2018, and pH, about 7.3 in 2017 and 7.4 in 2018." Readers have no idea what depth you are referring to. There is no figure versus depth for these parameters

"The main changes between the two campaigns correspond to a greater oxygen penetration in 2018, preventing nitrite accumulation and to the appearance of a surface layer (with salinity below 3) that stands above the primary production zone in 2018." Readers are lost not only because figures are not showing what you are referring to, also because you show and discuss the data at the same time.

L172 "Because of the presence of oxygen, the NO<sub>2</sub><sup>-</sup> production would be more likely associated with nitrification of the NH<sub>4</sub><sup>+</sup> diffusing upward rather than denitrification despite the possibility of reducing conditions occurrence in micro niches." No NH<sub>4</sub> and NO<sub>3</sub> data are shown, it looks speculative.

L178 "The MnO<sub>x</sub> decrease fits perfectly to the Mn<sup>2+</sup> increases in sulfidic conditions (Fig. 2)". sorry, I could not find this perfect fit in the sulfidic zone in Fig.2

L180 "efflux" > "flux"

End of page 7: you are discussing analytical aspects in a section about vertical stratification. This section is very difficult to follow. Rewrite.

L192 "However, due to river mixing with ocean waters..." the paper appears very confusing when it aggregates all mixing processes, spatial and time scales: longitudinal and vertical, seasonal. What are the typical vertical and longitudinal mixing times? I guess if the vertical structure is stable over time as the authors write, then vertical mixing is slow and the described geochemical reactions occur at timescales of months to year? This is what justifies the use of a single plot that aggregates the two seasons? Then the longitudinal mixing with seawater is not sampled here (salinity > 20) but it could be shorter? Mixing of buffered marine water with anoxic bottom waters (and thus reoxidation reactions) at low river flow and mixing with surface fresher waters at high river flow?

L197 "This offset is within the uncertainty of the endmember calculation even if slight DICex background enrichment has been modelled (Shen et al., 2019) resulting from faster atmospheric equilibration of O<sub>2</sub> than CO<sub>2</sub> after respiration reactions." Not clear what you mean here: what has DICex enrichment to do with different rates of CO<sub>2</sub>/O<sub>2</sub> atmospheric exchange? Please explain. This is a classical problem when results are mixed with discussion. The amount of data presented and the relative complexity of the geochemical analysis make the combination of result and discussion sections very difficult to follow.

What is the point discussing these values of freshwater end-member? all the reactions described in the paper occur at salinity >1.7 or 7.1, so this salinity value can be used as end-member. Extrapolating all TA values until Sal 1.7 (high river flow) as done in the MS is ok if vertical mixing time, no need for a long text about the choice of FW end-member, same for SW. Describe in Mat & Met

Fig 3 panel c: arrow direction "CO<sub>2</sub> uptake" would decrease DICex, not increase

L200 "Interestingly, the relative changes of DICex and TAex, further named  $\Delta$ TAex and  $\Delta$ DICex, does not depend on the endmember calculation and their ratio presents much lower uncertainties (about 0.1) facilitating their interpretation". This could be partly transferred to the Mat & methods section. A scheme in a suppl. figure could also help to define the variables along the vertical salinity gradient.

L200 "In 2017, TAex stayed almost constant up to the oxic zone (Fig. 3a)" we cannot see the "oxic zone" in Fig 3a, only guess it. Result section could show depth profiles and discussion the salinity plot

" $\Delta$ TAex/ $\Delta$ DICex ratio of  $0.1 \pm 0.1$  which indicates a net aerobic respiration (AR)" not only respiration, also primary production assimilating NH<sub>4</sub><sup>+</sup>. What is a "net" aerobic respiration?

What has the discussion in L200-L220 to do with "river flow control", the title of the section? The MS needs to be reorganized.

L210 "Finally, for 2017, despite pCO<sub>2</sub> being below atmospheric saturation at about 2 m depth (Fig. 1), the possible CO<sub>2</sub> invasion does not significantly modify the observed  $\Delta\text{DIC}_{\text{ex}}/\Delta\text{AOU}$  signal at the shallowest depth sampled." I agree that gas exchange is a slow process compared to PP and AR. However, gas exchange still occurs and it affects DIC/AOU ratio with a slope still close to 1

L215 "In 2018, this surface water history did not repeat as fresh and light water masses brought by the exceptional flood drastically modified the carbonate system equilibrium. First, a low salinity layer with pCO<sub>2</sub> at 1000  $\mu\text{atm}$  overlays the primary production layer (Fig. 1)" We really need to see the most relevant vertical profiles.... Or isolines.

L217 "Just below the air-sea interface, the lock down of atmospheric exchanges by the low salinity layer produces supersaturation of trapped O<sub>2</sub> (Fig. 1, for S between 3 and 4)." Exhausting to follow. Contrarily to the authors, the reader has not seen the vertical profiles before. Low salinity > high salinity

"In Fig. 3a and 3b, this process translates into a vertical distribution at  $\text{DIC}_{\text{ex}} = 40 \mu\text{M}$  associated with negative AOU and slightly positive TA<sub>ex</sub>." I see no "vertical distribution" in Fig 3. Negative AOU is nothing special in surface productive waters

L219 "This original signature can be modelled by the combination of simultaneous carbonate dissolution (CD) and PP fuelled by NH<sub>4</sub><sup>+</sup>, in equal proportion and would result in no  $\text{DIC}_{\text{ex}}$ , only TA<sub>ex</sub> production (see Table 2); the carbonate dissolution buffers the DIC consumption produced by PP. The Ca<sup>2+</sup> concentrations observed by Su et al. (2021) and during the 2018 cruise (data not shown) vary linearly with salinity i. e.  $[\text{Ca}^{2+}] = 0.282 S + 0.4$  in mmol L<sup>-1</sup>. Assuming similar behaviour in 2017, calculations show that the whole water column is undersaturated with respect to calcite and validates the possibility for CD." This seems speculative (no calcite saturation value is shown); in general, PP increases the pH and favours CaCO<sub>3</sub> precipitation rather than dissolution. One could also say that if Ca<sup>2+</sup> is conservative, then little or no precipitation/dissolution occurs.

L220-230 are difficult to follow; this section starts identifying some preponderant reaction at the top of the water column (oxic condition, what about reoxidation of reduced species diffusing from below?), but the following section is entitled "Identification of preponderant reactions". The paper needs a better organisation

There seems to be a mistake in reaction SR-O In table 1, H<sub>2</sub>SO<sub>4</sub> appearing on both sides

of the arrow. If you eliminate H<sub>2</sub>SO<sub>4</sub>, then the reaction is aerobic oxidation. In fact you cannot combine two reactions when one occurs only in oxic condition and another only in anoxic condition

L235 remove "3.3. Sediment control"

L238 "cannot be explained by most typical chemical reactions such carbonate dissolution (CD), aerobic respiration (AR), CO<sub>2</sub> uptake or primary production (PP = -AR)." I thought this section concerned anoxic conditions. This is confusing

L241 "Moreover, SR alone underestimates the importance of the H<sub>2</sub>S oxidation pathway." Not sure what you mean here, please reword

L246 "Middelburg et al., 2020" many typos in the MS

L248 "corresponds to the uncharged species produced, mostly in solid or gaseous phases" be precise... you mean N<sub>2</sub> by denitrification and FeS ?

L257 "a non-charged species." > specie

L260 reasoning on the importance of N based only on NO<sub>2</sub><sup>-</sup> data looks speculative if no NO<sub>3</sub><sup>-</sup> / NH<sub>4</sub><sup>+</sup> are shown

Fig4: show all units

L263-266 Suddenly, the authors mention a "monthly timescale" without any apparent reason for that.

L267 " "important" stock concentrations at a monthly timescale (with concentrations that frequently exceed 1 mM in anoxic porewater)." Why porewater? The study does not deal with sediment

L272 "represent the main expected respiration processes" please better explain why the 2 mentioned reactions are expected to predominate. Why Mn more than Fe?

L270-285 contains many shortcuts and language imprecisions and hardly convince the readers that the mentioned reactions are preponderant. The analysis appears almost only qualitative, based on TA/DIC ratios, not quantitative based on concentrations and mass-balance

"The reduction of  $\text{HNO}_3$  down to  $\text{NH}_3$  is not detailed but would result in almost similar alkalinity changes: 1.15 for  $\text{NH}_3$  production (DNRA) versus 0.95 for  $\text{N}_2$  production." Instead of "alkalinity changes", do you mean TA/DIC ratio?

"The only solid form of Mn(II) is  $\text{MnCO}_3$ , since  $\text{MnS}$  is negligible" why should Mn(II) be solid? Unclear. In fig 2 max Mn(II) concentration is about 8  $\mu\text{M}$  in the bottom layer, how does this contribute stoichiometrically to the 100  $\mu\text{M}$  increase of TA?

L275 " $\text{FeCO}_3$  production would produce a very similar reaction as  $\text{MnCO}_3$  production; the latter, more common, is favoured in this simple description." What "simple description" are you referring to here?

L277 "minimum required amount of sulfate reduction" Awkward formulation improve language

L280 "After sulfate reduction,  $\text{H}_2\text{S}$  can also accumulate in the water (SR reaction) or be oxidized back to  $\text{SO}_4^{2-}$  (SR-O is detailed as an example)." Yes indeed. However,  $\text{H}_2\text{S}$  oxidation by  $\text{O}_2$  will lead to zero delta DIC and negative delta TA, and would result in an increase in the observed dTA/dDIC slope without the necessity of involving Mn secondary reactions. If  $\text{H}_2\text{S}$  is totally reoxidized by  $\text{O}_2$ , then the overall delta TA is null.

L285. Readers need to know to what redox zone you are referring to. This 2.4 slope concerns only the suboxic-sulfidic transition zone. In general, the paper needs a better organization and more detailed discussion.

L310-320 seems speculative and is not convincing: in the water column the quantities of Mn is not sufficient to validate the stoichiometric model. Why should the reaction occur in the sediment, if the 2.4 TA/DIC slope concerns the bottom of the water column and not the sediment porewater?

"The sedimentary solid Mn stock is about 10 mM" per square meter, per kilogram?

“which largely exceeds the 88  $\mu\text{M}$  required to produce the 100  $\mu\text{M}$  TAex increase.” The TA increase occurs in the bottom waters, if you want to relate it quantitatively to the sediment content, you should not only compare concentrations, but rather upward and downward fluxes in the bottom layers and at the sediment-water interface.

L320-326 are disconnected from the rest of the paper