

Reviewer #1

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 MnO₂ 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.

The “mistakes on the principles of carbonate chemistry” will be debated below.

The figures of poor quality not appropriate to describe the processes probably refers to the misunderstanding that all the data come from only one station

The figures of poor quality have been improved

The conclusions are based on observations clearly reported in the data i.e. $\Delta TA_{ex}/\Delta DIC_{ex}$ of 2.4 and the important MnO₂ recycling and intensively discussed in the manuscript. It seems that the reviewer does not get the reasoning exposed in this ms, probably due to many shortcut and lack of detailed explanations provided. The revised version improves it a lot

Main problems:

1-presentation

Presentation of the results is confusing and the MS structure with a “result and discussion” section makes it worth.

Result and discussion have been written again and are now separated

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.

Each sampling period was presented in its own graph in Fig 1, there is no aggregation between the two sampling period. The revised caption state it clearly. Plot against salinity bring better view of the water column stratification since it follows the water masses based on their density. As proposed by the reviewer 2, an additional figure plotting salinity and temperature against depth has been added (Figure 2); an additional Appendix (Fig. A2) plots O₂, pH, H₂S, pCO₂, TA_{ex} and DIC_{ex} against depth has been added.

Conceptually, longitudinal gradients are mixed with vertical gradients without any consideration about respective mixing times.

Longitudinal gradient are not mixed with vertical gradient because all the samples are from the same station: Station 858. This information has been underlined in the revised version and is now repeated regularly including in section title, to avoid any misunderstanding.

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.

The word freshwater is not written in this manuscript, we clearly call it upstream estuary endmember. In the section 2.3.1 only 10 lines are now devoted to the endmember selection (versus 21 lines in the previous version) and more precision about the hypothesis required for the “reaction driven” interpretation were added. However, we think that the discussion about endmember selection is critical for the paper as the main data interpreted are DIC_{ex} and TA_{ex} that vary based on the endmember selected. The definition of these endmembers can have impacts on all the dataset and requires careful definition.

We have no map of the estuary with sampling points.

It is because only one station has been sampled. The ms has been revised to highlight this important point.

No info about timescales, mixing of end members is analysed with little information about the timescale for the mixing to occur.

Mixing are estimated based on salinity that is conservative and assumption of steady state is now clearly explicit.

I was disappointed by the absence of real vertical profiles (some are in Fig A2, but not DIC and TA, pCO₂, 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)

An additional figure plotting salinity and temperature against depth has been added (Figure 2); An additional Appendix (Fig. A2) plots O₂, pH, H₂S, pCO₂, TA_{ex} and DIC_{ex} against depth has been added.

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 pCO₂ and O₂ %sat values at the surface, gas exchange can alter the AOU/EDIC ratio away from 1. Deviation of the O₂ / CO₂ correlation can be due to carbonate buffering effect on CO₂ but not on O₂ (see e.g. in rivers: Stets et al. (2017), doi:10.1002/2016GB005578.).

Gas exchange cannot be taken into account in the “reaction driven” interpretation since gas exchange does not follow a fixed stoichiometry but depend of the extent of a disequilibrium. We now explicitly point out this assumption and focus the discussion below 3-meter depth.

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 pCO₂ value at the surface, it would be possible to calculate the change in DIC due to invasion of atmospheric CO₂ in the first meters of the water column during the representative mixing time, and show that this change is negligible.

Water atmosphere exchange have been extensively investigated by Chen et al. 2020 on the Chesapeake Bay. In our case, it would be only possible for the 2018 campaign but is beyond the scope of our study. At 3-meter depth and below it can be considered 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.

Both are considered in the stoichiometric approach (see Table 1). However, since our dataset indicates that only the manganese seems important in our study case, we modify the title.

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.

When the reactions occurring in the suboxic or sulfidic zone during a water mass journey are combined together, it results overall in a few possible budget reactions that we summarized in the Table 1. Such approach has been already used in porewater by Rassmann et al. (2020) or in the water column by Hiscock and Millero (2006). We agree that even in these two publications, the assumption require for such approach where not explicitly described. Therefore we added a section 3.2.1 to trigger the condition where this approach (called “reaction driven” interpretation) is valid. The beginning of the discussion (section 4.1) focus on the applicability of the “reaction driven” interpretation on the station 858 in particular:

“Assuming 1) that mixing is efficiently described by turbulent diffusion mixing, 2) that the measured concentrations correspond to a steady state, 3) that the concentration at the starting point does not vary with time and 4) that the samples are isolated from atmospheric exchanges; the “reaction driven” interpretation (section 2.3.1) permits interpretation of the concentration changes as a linear combination of the stoichiometry of several chemical reactions (equation 5).”

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.

The “reaction driven” interpretation does not describe what is currently occurring at a given location but it describes the dominant reactions that modify a water mass chemistry during its overall journey since its equilibrium with the initial endmember. So it does account for secondary reactions that decrease the TA without changing the DIC. In particular, if H₂S diffused and is reoxidized by oxygen forming SO₄²⁻ the TA will decrease without changing the DIC. Therefore, the signature of a water mass submitted to sulfate reduction then to oxygenated oxidation will correspond to the signature of sulfate reduction plus the signature of oxygenated oxidation. It results in a signature similar to aerobic respiration (change of TA and DIC) that is taken into account in our description. We hope that the new version of the manuscript explain it better now.

Finally, the MS itself reveals the weakness of the conclusion about the importance of Mn reactions: L310 “Based on an average concentration of 20 μmol g⁻¹ of Mn in suspended particles, the 88 μM of MnO₂ would require a suspended material concentration of about 4.4 g L⁻¹, which is again one or two orders of magnitude higher than the 0.01 – 0.1 g L⁻¹ usually found in the Chesapeake Bay.”

We took special care to explicitly describe the boundary of our model and push it into its limitation, including saturation index calculation and mass balance calculation to validate the “reaction driven” interpretation. We explain the difference between Mn pool and TA pool by the role of sediment reactivity.

Line by line comments

Abstract

« burial of carbonate which modulates the ability of the ocean to trap anthropogenic CO₂. ». Not clear if you refer to build up of alkalinity in the ocean, which is indeed a sink of atmospheric CO₂ or burial of CaCO₃ which leads to degassing of CO₂ (Buffer factor 0.7, See works by Frankignoulle and Gattuso end of 90s in coral reefs). burial of carbonate would not trap anthropogenic CO₂.

The citation should include the subject of the verb : “The coastal alkalinity cycle controls the global burial of carbonate which modulates the ability of the ocean to trap anthropogenic CO₂”, to clarify the sentence we change it into: “The alkalinity dynamic in coastal environments controls the global burial of carbonate and modulates the ability of the ocean to trap anthropogenic CO₂”

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

You mention carbonate dissolution, but no precipitation occurs for instance in blooms at the surface? Precipitation was not visible based on the “reaction driven” approach and was probably only of minor importance, if any. The observed zone of primary production is at the subsurface as now clearly state

L28 “weathering” rather than “erosion” changed

“enrichment not associated with a Ca²⁺ enrichment, in contrast to the HCO₃⁻ released from continental erosion (preponderant at thousands to a million year scale, Urey, 1952).” HCO₃⁻ also comes from dissolution of continental rocks others than carbonate rocks (100% atmospheric CO₂), and thus without Ca²⁺ enrichment.

It seems that the reviewer refer to MORB degassing, whose part can occur during igneous rock weathering, we change the sentence in . “At the century time scale, atmosphere-ocean exchanges result in oceanic HCO₃⁻ enrichment not associated with a cationic enrichment, in contrast to silicate or carbonate weathering (preponderant at thousands to a million year scale, Urey, 1952)”

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 Some examples are presented in the Appendix Figure A3

Introduction is focussed on CaCO₃, 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. It is done in the section 2.3.1 of the new version.

L49: eleven or “a dozen”? “a dozen” has been removed from the manuscript due to its lack of precision

L62 define DI done

L93 “an excel sheet implemented with values from (Millero, 1995)” > which carbonate and bicarbonate dissociation constants and solubility coefficient of CO₂ ? We clarify this part : “The pCO₂, calcite saturation and TA were calculated from measured DIC and pH via CO₂sys program using Cai and Wang (1998) constants.”

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. We now clearly precise that the discussion is focussed below 3 meter depth away from atmospheric exchanges

L108 “Such changes were not necessary for DIC_{ex} calculation.” Why? The choice of the freshwater TA & DIC end-members looks arbitrary. Please better explain. In theory, the sensitivity of calculated DIC_{ex} and TA_{ex} to the values in the freshwater end-members can be calculated

The DIC versus salinity plot has been added in the Fig. A1. We wrote again the explanation: “the oceanic endmember was the one proposed by Su et al. (2020a) for August 2016 campaigns. Oceanic endmember varies mainly with season (Cai et al., 2020) and a change of 50 μM results in 5% uncertainty on the slope of the mixing line. Large variations exist in the

upstream estuary endmember mainly due to changes of weathering intensity and riverine discharge (Meybeck, 2003; Joesoef et al., 2017) and a one-off endmember has to be determined by fit with the in situ measurements at the lowest measured salinity (Fig. A1).”

We also add a calculation for the uncertainty:

“The uncertainty of $\Delta TA_{ex}/\Delta DIC_{ex}$ is equal to the sum of the relative uncertainty of ΔTA_{ex} and ΔDIC_{ex} . Posing ΔTA the change of TA measured, ΔS the change of salinity and sml_TA , the slope of the mixing line for TA, we have $\Delta TA_{ex} = \Delta TA - sml_TA * \Delta S$. Uncertainty on ΔTA and ΔS are negligible face to the relative uncertainty of sml_ml and posing $\delta(x)$ the incertitude on x, we get:

$$\frac{\delta(\Delta TA_{ex}/\Delta DIC_{ex})}{\Delta TA_{ex}/\Delta DIC_{ex}} = \frac{\delta(\Delta TA_{ex})}{\Delta TA_{ex}} + \frac{\delta(\Delta DIC_{ex})}{\Delta DIC_{ex}} = \frac{\delta(sml_TA)}{sml_TA} + \frac{\delta(sml_DIC)}{sml_DIC} = 0.1 \quad (6)$$

“

L111 “the uncertainty of our description” Awkward formulation **changed**

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.

We add a figure with the temperature and salinity against 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?

It is now explained: “Plots against depth generate noisier profiles are shown in Appendix 2 while plots against salinity follow the water masses.” **Indeed, between each sampling the water masses move due to tidal and river currents and are not located exactly at the same depth from one cast to another.**

L152 > “River” flow **changed**

L158 “Below, with increasing depth, an important increase of pCO₂ accompanying the decrease of O₂, 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, O₂, pCO₂ are shown.

The new result section clarifies these points.

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

The main goal was not to describe the air-water exchange. Thus we show the data when available (below 3 meter depth in 2017 and below 0.8 meter depth in 2018) but we focus the discussion on the redox gradient.

L159: “A relatively invariable low O₂ zone (called ILO in Fig. 1) is here defined by the depth invariance of O₂ 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 pCO₂, 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

We change “depth invariance” by “salinity invariance”.

“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.

Result and discussion are now separated

L172 “Because of the presence of oxygen, the NO₂⁻ production would be more likely associated with nitrification of the NH₄⁺ diffusing upward rather than denitrification despite the possibility of reducing conditions occurrence in micro niches.” No NH₄ and NO₃ data are shown, it looks speculative.

Replaced by “Below, a low oxygen layer with invariant concentration of most species survey (the ILO zone) is characterized by significant nitrite accumulation in 2017 probably due to oxidation of NH₄⁺ diffusing upward (Fig. 3).”

L178 “The MnOx decrease fits perfectly to the Mn²⁺ increases in sulfidic conditions (Fig. 2)”. sorry, I could not find this perfect fit in the sulfidic zone in Fig.2

Replaced by “the MnOx disappearance corresponds to the Mn²⁺ increases”

L180 “efflux” > “flux” the sentence has been removed

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

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?

As precised previously, there is only vertical variation reported in our publication for two summer in August 2017 and August 2018. Season are not aggregates. The new version clarifies this point.

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 O₂ than CO₂ after respiration reactions.” Not clear what you mean here: what has DICex enrichment to do with different rates of CO₂/O₂ 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. **This side interpretation has been removed to discard any discussion about air-water exchange that were not well constrained in our sampling design.**

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 **done**

Fig 3 panel c: arrow direction “CO₂ uptake” would decrease DICex, not increase

The arrow has been removed to focus on redox reaction in the water column, but from a water column point of view, uptake suggests that this is an uptake from atmosphere into the water column, so it increases DICex.

L200 “Interestingly, the relative changes of DICex and TAex, further named ΔTA_{ex} and ΔDIC_{ex} , 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. **We add a figure in the section 2.3.1 that explicitly describe the condition for the “reaction driven” interpretation**

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

We can easily infer where is the oxic zone looking at a Figure plotting apparent oxygen uptake.

“ $\Delta TA_{ex}/\Delta DIC_{ex}$ ratio of 0.1 ± 0.1 which indicates a net aerobic respiration (AR)” not only respiration, also primary production assimilating NH₄⁺. What is a “net” aerobic respiration?

We agree that both AR and PP are characterised by the slope $\Delta TA_{ex}/\Delta DIC_{ex} = 0.1$, but since in our case it result in a increase of TAex it result in net AR (AR>PP). It is now precised in

section 4.1: “This interpretative framework describes the vertical stratification of the water column as the journey of a water mass slowly mixed deeper and deeper and whose DIC and TA are progressively enriched by all chemical reactions they undergo. Accordingly, this interpretation does not identify reactions with minor impact on the carbonate cycle or reactions cancelled later during the journey, for example, PP is frequently cancelled by similar amount or excess of AR.”

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

L210 “Finally, for 2017, despite pCO₂ being below atmospheric saturation at about 2 m depth (Fig. 1), the possible CO₂ 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

Because gas exchanges are proportional to the disequilibrium it does not result in a fix DIC/AOU ratio and is therefore not considered in the “reaction driven” interpretation.

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 pCO₂ at 1000 μatm overlays the primary production layer (Fig. 1)” We really need to see the most relevant vertical profiles.... Or isolines. **Now available in Figure A2**

L217 “Just below the air-sea interface, the lock down of atmospheric exchanges by the low salinity layer produces supersaturation of trapped O₂ (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 > low 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_{ex}.” I see no “vertical distribution” in Fig 3. Negative AOU is nothing special in surface productive waters

An arrow show the vertical distribution of TA_{ex} and AOU. It is not particularly special, it just reflects the reaction CD-AR (table 2)

L219 “This original signature can be modelled by the combination of simultaneous carbonate dissolution (CD) and PP fuelled by NH₄⁺, in equal proportion and would result in no DIC_{ex}, only TA_{ex} production (see Table 2); the carbonate dissolution buffers the DIC consumption produced by PP. The Ca²⁺ 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⁻¹. 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 CaCO₃ precipitation rather than dissolution. One could also say that if Ca²⁺ is conservative, then little or no precipitation/dissolution occurs.

Thanks to this comment, we take a more careful analysis to the Ca²⁺ profile. It came out that “The Ca²⁺ concentrations observed by Su et al. (2021) and during the 2018 cruise (data not

shown) vary linearly with salinity. Assuming similar behaviour in 2017, calculations show that the whole water column (except 4 samples from the PP zone) is under saturated ($0.36 < \Omega_{cal} < 1$; mean=0.68) with respect to calcite in 2018, while undersaturation is only valid below $S=10$ in 2017.”

In this part, we have to explain an increase of TA, a decrease of AOU and no DIC changes. Which fit with CD and PP. In this layer, the calcite saturation increase up to saturation for the 4 points with higher pH. It is thus possible to have a bit of precipitation in a thin layer, but it does not overwhelm the signature of carbonate dissolution that occur previously in these water mass.

Ca^{2+} concentration vary linearly with salinity in our sample, but, compare to the mixing line between estuarine and oceanic water it corresponds to a Ca^{2+} excess of up to 200uM.

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. **We hope that the new organisation make the reading easier.**

There seems to be a mistake in reaction SR-O In table 1, H_2SO_4 appearing on both sides of the arrow. If you eliminate H_2SO_4 , 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.

It is sure we can combine two reactions occurring in different conditions, as soon as a mixing makes possible the transfer of the solutes at similar rate which is the case with turbulent diffusion.

L235 remove “3.3. Sediment control” **done**

L238 “cannot be explained by most typical chemical reactions such carbonate dissolution (CD), aerobic respiration (AR), CO_2 uptake or primary production ($PP = -AR$).” I though this section concerned anoxic conditions. This is confusing

Removed

L241 “Moreover, SR alone underestimates the importance of the H_2S oxidation pathway.” Not sure what you mean here, please reword

The new version is :

Moreover, SR alone underestimates the importance of the H_2S oxidation pathway that can consume all the alkalinity produced during SR. For example, SR follow by oxygenated oxidation results in $\Delta TA_{ex}/\Delta DIC_{ex}/\Delta AOU$ signature equal to AR only. In the Chesapeake Bay, H_2S oxidation is critical since no H_2S is measurable in the suboxic zone while the gradient at the sediment/water interface indicates high H_2S sedimentary efflux (Fig. 3).

L246 “Middelburg et thal., 2020” many typos in the MS **changed**

L248 “corresponds to the uncharged species produced, mostly in solid or gaseous phases” be precise... you mean N₂ by denitrification and FeS ?

it can be N₂, N₂O, CO₂, FeS FeS₂ FeOOH MnO₂ CaCO₃ we stay general to not be too specific and precise later in the ms and in Table 1

L257 “a non-charged species.” > specie **this sentence has been removed**

L260 reasoning on the importance of N based only on NO₂- data looks speculative if no NO₃- / NH₄⁺ are shown

It is now stated: Therefore, in the absence of nitrate, oxygen and H₂S,

Fig4: show all units **this figure has been removed**

L263-266 Suddenly, the authors mention a “monthly timescale” without any apparent reason for that. **Replaced by** at steady state

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 **changed into** anoxic water

L272 “represent the main expected respiration processes” please better explain why the 2 mentioned reactions are expected to predominate. Why Mn more than Fe? **Because the admitted form of Fe is FeS or FeS₂ that can be only produced with sulphide.**

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 HNO₃ down to NH₃ is not detailed but would result in almost similar alkalinity changes: 1.15 for NH₃ production (DNRA) versus 0.95 for N₂ production.” Instead of “alkalinity changes”, do you mean TA/DIC ratio? **This sentence has been removed**

“The only solid form of Mn(II) is MnCO₃, since MnS is negligible” why should Mn(II) be solid? Unclear. In fig 2 max Mn(II) concentration is about 8microM in the bottom layer, how does this contribute stoichiometrically to the 100 microM increase of TA? **The discussion based on mass balance is now presented in the dedicated section 4.5**

L275 “FeCO₃ production would produce a very similar reaction as MnCO₃ production; the latter, more common, is favoured in this simple description.” What “simple description” are you referring to here?

The above remarks correspond to a section that has been re written and is now:

To build a pool of candidate reactions for the fitting, first, dissolved species at too low concentration (e.g. Mn²⁺aq, Fe²⁺aq) to be a net reagent to affect the carbon cycle at steady state are not taken into account. These species are usually recycled rapidly and hold a role of catalyser or electron shuttle between other redox species. Second, many mineral expected at low concentration or thermodynamically not favoured and their associated reactions are

neglected (e.g., iron phosphate, ferrous or manganous oxide, sulphur clusters, MnS, FeCO₃, adsorption processes, reverse weathering). Therefore, only aqueous species with important stock concentrations (that can exceed 1 mM in anoxic water) are taken into account, i. e., SO₄²⁻, Ca²⁺, H₂S, NH₄⁺ together with gaseous (N₂, CO₂) and main solid phases (FeS₂, FeS, S₀, MnCO₃, FeOOH, MnO₂). Third, many combination of carbon remineralisation reaction with a re-oxidation reaction are equal to another remineralisation reaction. As an example, SR follow by H₂S oxidation with oxygen is equal to aerobic respiration.

L277 “minimum required amount of sulfate reduction” Awkward formulation improve language **this sentence has been removed**

L280 “After sulfate reduction, H₂S can also accumulate in the water (SR reaction) or be oxidized back to SO₄²⁻ (SR-O is detailed as an example).” Yes indeed. However, H₂S oxidation by O₂ 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 H₂S is totally reoxidized by O₂, then the overall delta TA is null.

If H₂S is totally reoxidized by O₂ after sulfate reduction, the overall Δ TA is 0.15 due to ammonium release, Δ DIC is 1 and Δ AOU is 1 exactly as if it was aerobic respiration (Table 1). It is not involving Mn secondary reaction but is not able to explain the Δ TA_{ex}/ Δ DIC_{ex} of 2.4.

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 reaction should occur in the sediment because the quantities of Mn in the water column is not sufficient to validate the stoichiometric model. Because the Mn product is solid it would have stay in the sediment while the Δ TA_{ex}/ Δ DIC_{ex} fingerprint would have been able to diffuse out of the sediment into the water column with other reduced species as the redox front move up when the summer start.**

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

mM is mmol L⁻¹ per liter of porewater

“which largely exceeds the 88 μ M required to produce the 100 μ M TA_{ex} 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.

We agree that a direct flux measurement will give more convincing argument. Therefore we can only say that it is possible. We try to find the more likely explanation to an observable. Accordingly we use conditional formulation .

“Therefore, the Chesapeake Bay sediment is particularly rich in manganese and could host important SR-MnC reactions in the superficial pore water whose soluble products diffuse up to the water column during summer could bear with them the high $\Delta TA_{ex}/\Delta DIC_{ex}$ signature observed.”

L320-326 are disconnected from the rest of the paper

This section proposes to upscale the process observed in the Chesapeake Bay at the global scale.

Reviewer #2 :

General comments

Thibault de Chanvalon et al. have written a manuscript describing carbonate system dynamics in the Chesapeake Bay. The originality and novelty of the manuscript lies in the high-resolution measurements of iron and manganese species in Chesapeake Bay, of which the carbonate system dynamics have long been investigated by the senior author. However, the finding that Mn dynamics are most important for explaining the observed trend in ΔTA_{ex} to ΔDIC_{ex} does not seem to be substantiated by the manuscript in its current form.

In particular, section 3.3 contains many assumptions that are not substantiated by measurements or modelling

We still believe that an approach based on linear combination of reaction stoichiometry is valid. A new section (2.3.1 *Identification of biogeochemical process from scatter plot: the hammer, the bow and the spear*) focusing on possible interpretations of a scatter plot of two species now describes more precisely the assumption required.

...and in which a discussion on reaction kinetics is missing. For example, it is discussed in section 3.2 that slow reaction kinetics of nitrification may explain the lack of signal here, but there is no mention of kinetics impacting any of the (net) pathways in section 3.3. I think, however, that given the truly dynamic nature of the study site, kinetics may be key in explaining the observed trends, and that it may not be possible to do this using linear combinations of reaction equations and stoichiometry.

We agree that kinetic consideration may be a key in explaining why such a reaction is preponderant over another one, thermodynamic being the second key. It is implicitly taken into account in our model by the coefficient of the linear combination, the section 2.3.1 now clearly explains how. By the way, this stoichiometric approach has already been applied to water column without extensive justification (e.g. Hiscock and Millero, 2006).

The introduction solely focuses on carbonate precipitation and dissolution, whereas the manuscript has a much broader focus and also investigate the role of the Fe and Mn cycles. I would encourage the others to expand the introduction by at least one paragraph explaining the role of other elemental cycles in alkalinity dynamics. This also makes a better transition towards explaining the aim of this study.

We added new section in the introduction

I do not advocate a combined results and discussion and especially in this manuscript it leads to confusion on what is interpretation and what is not. It shouldn't be too difficult to separate both sections.

Result and discussion have been separated and write again

The conclusions on the important role of Mn at this site are rather speculative and contain references to other study that belong in the discussion.

Conclusion has been deeply reworked in order to focus on demonstrated results and clearly specify what belong to hypothesis, in particular to the "reaction driven" interpretation.

The manuscript is generally written in a sloppy way. I stopped identifying typos already early on, simply because there are so many. So please do a proper check on this for a next version.

Also, there are many exceptionally long sentences. This makes it difficult to following reasoning. At this stage, I'm afraid I cannot recommend anything else but a rejection. I do encourage the authors to rework the manuscript into a better one, because the data underlying the manuscript are interesting and of high quality.

Minor and technical comments

L. 12 (and other places): I do not like the term “alkalinity cycle” too much. This suggests the cycling of a particular element (e.g. C) whereas alkalinity dynamics are the result of the cycling of many different elements.

This term has been changed into “The alkalinity dynamic in coastal environments ... »

L. 19: What do $\Delta\text{DIC}_{\text{ex}}$ and $\Delta\text{TA}_{\text{ex}}$ mean? Better not to use these abbreviations in the abstract.

These abbreviations have been deleted and replace by : “In oxygen depleted waters, 2.4 mole of DIC is produced per 1 mole of TA production. This substantial DIC increase relative to TA has not been previously reported in the literature, and is consistent over the two years”

L. 25: This is not a citation to the most recent global carbon budget. Also, estimates of the last decade mention that ca. 25% of anthropogenic CO₂ has been absorbed by the oceans, not 33%.

More recent reference was add (Friedlingstein et al., 2022) instead of (Friedlingstein et al., 2019), in which they precise that 29.5+-5% of anthropogenic CO₂ has been adsorbed by the oceans. It is now precised “30%”

L. 31: “shallow waters” **corrected**

L. 32: “carbonate dynamics” **corrected**

L. 39: not sure why specifically HCO₃⁻ dynamics is used here. Isn't this more generically carbonate system dynamics? **We delete this part of the sentence**

L. 48: “sampling campaigns” (I stopped identifying typos here as there are too many) **corrected. All the typos have been review again to limit the errors.**

L. 49: What is meant here, at 25-m water depth, or at a location with a water depth of 25-m? I assume the former, but please write more clearly (also in L. 54-57). **It is now written:** “eleven profile casts were conducted in a unique station in the Chesapeake Bay with a water depth of 25 m »

L. 65-85: this is not written in a very engaging way.

L. 91-92: Which CRMs? **It is now precised**

L. 92-95: Why wasn't CO₂sys used from the start? I'd say that it is common practice to use one of the packages for carbonate system calculations. And which equilibrium constants were used? Also, which other acid-base systems were taken into account? That matters for your conclusion that organic alkalinity is irrelevant in this study. In summary, this section severely lacks detail.

This section was written again :

“The $p\text{CO}_2$, calcite saturation and TA were calculated from measured DIC and pH via CO2sys program using Cai and Wang (1998) constants. The measured TA was found highly correlated to the calculated TA ($r^2 = 0.995$ and 0.998 , slope = 0.995 and 1.017 for 2017 and 2018 campaign respectively) and their difference was always below $30 \mu\text{M}$ with an average of $7.5 \mu\text{M}$ for 2017 and of $22.2 \mu\text{M}$ in 2018. These results suggest low contribution of non-carbonate species (e.g. nitrite, ammonium or organic matter (Cotovicz Jr. et al., 2016)) and measured TA was used for the interpretation.”

L. 103-110: The choice of the alkalinity freshwater endmember is extensively explained but I am not 100% convinced about it. Assuming there was some biological activity between $S=0$ and $S=1.5$, and thus TA at $S=1.5$ is somewhat overestimated, how would that potentially affect the slope of the mixing line and consequently your excess TA?

There can be intense biological activity or weathering between $S=0$ and $S=1.5$, or even upstream in the river; what matter is the speed of variation of the endmembers. Especially if the riverine endmember changes faster than the water flow through the estuary. In our case it is safer to take an endmember at $S=1.5$ that represent a large pool of water in the Chesapeake Bay (with significant inertia) rather than the endmember at $S=0$ in the Susquehanna River that flow continuously and could change rapidly. The section 2.3.1 now clearly stipulates

“The upstream endmember is not a river endmember (Su et al., 2020a) but corresponds to a salinity above 1.5 preventing any interpretation for biological activity in the fresh water part of the estuary (Meybeck et al., 1988). However, it corresponds to a larger water mass pool, less sensitive to short term changes and thus more likely to satisfy the condition of stability of the endmember.”

The uncertainty related to the change of endmember is now presented in section 2.3.1:

The uncertainty of $\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}$ is equal to the sum of the relative uncertainty of $\Delta\text{TA}_{\text{ex}}$ and $\Delta\text{DIC}_{\text{ex}}$. Posing ΔTA the change of TA measured, ΔS the change of salinity and sml_TA , the slope of the mixing line for TA, we have $\Delta\text{TA}_{\text{ex}} = \Delta\text{TA} - \text{sml_TA} \times \Delta S$. Uncertainty on ΔTA and ΔS are negligible to the relative uncertainty of sml_ml and posing $\delta(x)$ the uncertainty on x , we get:

$$\begin{aligned} \frac{\delta(\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}})}{\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}} &= \frac{\delta(\Delta\text{TA}_{\text{ex}})}{\Delta\text{TA}_{\text{ex}}} + \frac{\delta(\Delta\text{DIC}_{\text{ex}})}{\Delta\text{DIC}_{\text{ex}}} \\ &= \frac{\delta(\text{sml_TA})}{\text{sml_TA}} + \frac{\delta(\text{sml_DIC})}{\text{sml_DIC}} = 0.1 \end{aligned} \quad (6)$$

L. 114: Section 2.3.2 does not deal with reaction stoichiometry; another title would be more appropriate

We now precise :

“From Eq. (12), one can easily deduce the changes of alkalinity from any reaction stoichiometry as soon as the bearing charges at $\text{pH} = 4.5$ are known.”

L. 116-140: Rather than defining a new equation and terminology, why not use either of the existing frameworks and corresponding terminologies of either Soetaert et al. (2007) (excess negative charge) or Wolf-Gladrow et al. (2007) (explicit conservative expression). The

framework of Soetaert et al. (2007), specifically the definitions in section 3.3, seem as generic as the equations defined here because additional species can be included.

Reviewer #2 considers that the terminology proposed by Soetaert et al (2007) is as generic as the former equation (4), now improved into the equation (12). The Soetaert et al (2007) publication was a fantastic source of inspiration, nevertheless their definition of alkalinity is based on the excess of negative charge plus/minus six specific chemical species:

$$TA = \Sigma[-] + \Sigma NH_3 - \Sigma NO_3 - \Sigma NO_2 - \Sigma PO_4 - 2 \Sigma SO_4 - \Sigma F \quad (A1)$$

With $\Sigma [-]$ being the sum of total charge of all the acid-base species. Which requires first to identify all acid-base species and second to know the exact charges they bear at the sample pH (Fig 1B from the publication can help you) which is much less synthetic than our equation (4) from the original manuscript and than the equation 12 of the current manuscript. $TA = \Sigma z^{pH=4.5}$

For example, the equation A1 does not allow the reader to easily understand how “new” species (such as reduced FeS clusters or DOM) will change the alkalinity, which is what our equation (12) does.

L. 141-146: It is completely unclear which reactions are referred to in this section. Specify / expand.

All this section has been expanded in section 2.3.1 to clearly justify the use a linear combination. Moreover, it is now precised “A limited number of reactions is selected as candidates based on the discussion (see Table 1 and sections 4.2 and 4.3).”

L. 149-152: I understand this choice but would be good to still show the plots versus depth as it is a more common way. Perhaps in supplementary information. Or show plots of salinity versus depth.

We add the Figure 2 of Salinity and temperature against depth. We also add the superimposed casts versus depth in Appendix 2 and some examples of individual cast versus depth in Appendix 3

L. 152: “the processes” – which ones? We now only stipulate that salinity follow better the water masses

L. 152: “overall much lower salinity”. Maximum values declined from ~20 to ~16, I wouldn't call that ‘much lower’ we deleted “much”

L. 155: atmospheric pCO₂ was likely higher than 400 uatm. We change this value by 407 uatm (Chen et al. 2020)

L. 162: I wouldn't call a zone with an oxygen concentration of less than 1 uM sub-oxic (I am in general not an advocate of this term), but rather anoxic Suboxic is use to differentiate this zone to the sulfidic zone (also anoxic)

Fig. 1: I am not sure how correct it is to use a linear transformation for plotting for a non-linear variable like pH This plot is only informative and does not contribute directly to any calculation, so the linear transformation is only functioning as a zoom.

L. 171-174: I can see this pattern in NO₂ in the 2017 data but not really in the 2018 data. Do you have an explanation for this? It is now precised in the first part of the discussion : “ the significant nitrite accumulation [...] is not visible in 2018 probably because the higher O₂

concentration in 2018 accelerate nitrite oxidation into nitrate and prevent any significant accumulation.”

L. 175: This reads a bit odd. I think what you mean to say is that any O₂ diffusing downwards would react with upwards diffusing Mn²⁺. **corrected**

L. 184: “emerging picture” **removed**

Fig. 2: mistake in caption; this is nitrite, not nitrate **corrected**

L. 200-207: If I remember correctly (I didn’t look it up), in the model used by Cai et al. (2017) their results were explained by combining aerobic respiration with nitrification. Can the authors elaborate on the comparison with this study? In general, to me it seems surprising that no nitrification would take place.

Cai et al 2017 does not invoke nitrification, in surface estuary nitrification is frequently considered negligible in regards to TA changes (see Abril et al. 2003 for example). Additionally, we never wrote that nitrification does not take place; it is just not enough important to significantly change the TA and DIC signature. However, in the ILO zone in 2018 our initial consideration that only AR occur can be improved by taking into account both CD and Nit, we added:

“Deeper, in the ILO zone, $\Delta TA_{ex}/\Delta DIC_{ex}/\Delta AOU = 0.2/1/1.25$ (Fig. 5a and 5b) results mainly from AR (0.15/1/1) with possible addition of CD and Nit, the exact signature being fitted for 0.54 CD and 0.46 Nit for 1 AR (4th line in Table 2), in close continuity of AR and CD relative rates from the overlaying layer. This important nitrification is also in good agreement with the lack of nitrite build up in the ILO zone and the relatively high oxygen concentration (at 105 μM) in the ILO zone in 2018 which is able to sustain nitrification.”

L. 216: “as was observed for other years” – including 2017 or not? **The surface sampling was not precise enough for 2017 cruise, but in august 2016 Chen et al. (2020) report pCO₂ below 300 μatm at station 858.**

L. 219 – 224: Good that saturation calculations were done here, although it would be good to actually present the (range of) values. Is there a logical source of calcite in this part of the Chesapeake Bay in 2017 that would support this hypothesis? (especially given what is written in L. 229 – 230).

Su et al 2021 report Ca²⁺ production for august 2016 indicating that carbonate dissolution can occur in the Chesapeake Bay. The calculation of carbonate saturation shows that undersaturation more pronounced in 2018 in agreement with the fact that the DIC/TA approach identify CD only for 2018. Section 3.1 explains:

“The Ca²⁺ concentrations observed by Su et al. (2021) and during the 2018 cruise (data not shown) vary linearly with salinity (calcium excess stay below 200 μM or 10% of total Ca). Assuming similar behaviour in 2017, calculations show that the whole water column (except 4 samples from the PP zone) is under saturated ($0.36 < \Omega_{cal} < 1$; mean=0.68) with respect to calcite in 2018, while undersaturation is only valid below S=10 in 2017.”

Also, are any analyses done on the type of algae that would contribute to PP? **we have not made any characterisation of primary producers.**

L. 237: “never reported in the literature” – perhaps in estuaries or using this particular metric or $\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}$ (although I am not even certain about this). But ratios of TA/DIC exceeding 2 have been discussed in earlier works.

We extended the bibliography to calculate $\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}$ in other environment and summarized it in the section 4.4, but ratio above 2.3 were not found in our short review. If the reviewer has the opportunity to send us any reference we could include them in the discussion.

L. 252 – 258: My main issue with this discussion is that there can be more fates of H_2S than only discussed here, each having a different $\Delta\text{TA}/\Delta\text{DIC}$ ratio. I am not sure that the choice of reactions discussed here and given in table 1 is properly substantiated, especially since no actual modelling has been conducted ...

We improve the discussion about the candidate reaction selection in the new section 4.3. About the fate of H_2S , we include reoxidation into sulphate or into S_0 precipitation as FeS or as FeS_2 ... to my knowledge it corresponds to the consensual main species H_2S can change in. We think the Table 1 well describe the possible fate of H_2S .

... and since solid S species or MnCO_3 have not been measured.

We agree that our publication would have been reinforced by S and MnCO_3 measurement on suspended material. However, we didn't initially expect that MnCO_3 would have an important role before sampling. Whatever, it would probably not change anything: as discussed, the MnCO_3 precipitation does not occur in the water column (TA build up is too important and Rhodocrosite is undersaturated) but in the sediment. The development of anoxia at station 858 corresponds to an upward diffusion of the redox front that with them the pore water TA and DIC signature. We add additional description about the Mn content in the Chesapeake sediment from other publications showing that Mn is very dynamic in the Chesapeake Bay and that important part of MnOx deposited rapidly turn into MnCO_3 .

As a result, the authors cannot state whether the formation of MnCO_3 is actually important in the Chesapeake Bay. In fact, the authors state this to some extent themselves in L. 269-270.

We clarify the writing to not state that MnCO_3 is important, but to only state that the model suggests that MnCO_3 is important... which is confirm from a sediment point of view by other publication.

L. 279: I don't understand the unit of $\Delta\text{TA}_{\text{ex}}$ here – or is something else meant? This has been removed.