

Review #2.1

The paper deals with a very important topic which is the transport and transformation of material in estuaries and the role of filter (or reactor) that these estuaries provide. Furthermore, the paper deals with one of the largest and the most studied estuaries on Earth (Chesapeake Bay) which is submitted to numerous anthropogenic pressures. Despite the previous papers including the recent ones by Su et al. (2020-2021), the carbonate system, which is the “currency” of all carbon exchanges in the aquatic environment is still poorly known.

Main comment: In the present paper, Thibault de Chanvallon et al. explore the role of metals (Fe and Mn) and in situ transformation in the carbon biogeochemical cycle. They spend a great deal of time (and text) to convince us that in situ transformations are happening and that the observed profiles (or pseudo- profiles as they are plotted against salinity and not depth) are due to complex transformations involving precipitation of carbonate (MnCO_3), several biogeochemical “suboxic” pathways with Fe and Mn, and some anoxic pathways. The demonstration is convincing (up to a certain point see comments below), but in a short final paragraph they admit that the biogeochemical reactions do not occur in the water column (hence not in situ) due to the lack of reagents (MnOx) or undersaturation with respect to MnCO_3 . According to them, these transformations rather occur in the sediments, and their by-products are then transferred to the water column. This is in complete contradiction with their statements (including the abstract) that the reactions occur in the water column and change its chemical composition. Furthermore, the paper provides no evidence that these reactions are occurring in the sediment (porewater or sediment profiles, incubations, ...). The authors should deeply rework their paper in order to include the benthic source of transformation from the start of the paper instead of stating that at the end.

The new version of section 2.4.1, better describes the conditions required for the “reaction driven” interpretation. It is now demonstrated that a straight line in a portion of a TA_{ex} VS DIC_{ex} scatter plot indicates that one local endmember has been previously produced from the other by a chemical reaction of $\alpha_{\text{TA}_{\text{ex}}}/\alpha_{\text{DIC}_{\text{ex}}} = \Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}$. (1157-162)

“However, in a stratified water column, not only one but several successive reactions occur, requiring many integrations of equation (3). On the boundary of each space portion with constant $\alpha_{\text{C}}/\alpha_{\text{D}}$, specific local endmembers are defined with concentrations at steady state fixed due to the ongoing reactions and not due to the inertia of large body of water. The general case is not straightforward to solve but in the particular case where the C versus D plot represents a straight line in a portion of space, the equation (4), still valid in each portion of space, indicates that $G=0$, thus that the local endmembers are maintained in steady state by a chemical reaction with a similar stoichiometry that the one that produced them, *i.e.* $\Delta\text{C}/\Delta\text{D} = \alpha_{\text{C}} / \alpha_{\text{D}}$.”

The short final paragraph indicates that the local endmember previously produced moved up as the summer begin has been rewritten. (See additional information in reviewer #2 answer.) Therefore, there is no anymore contradiction between the conclusion and the demonstration. The benthic source is now included from the start of the paper (including abstract).

Other Comments:

1- Illustrations: In general, the graphs are of poor quality and very hard to read. Figure 3 and 4 that present the main results of the paper are hard to read as the symbols are too small (and very often quite similar), and the axis should be splitted in multiple axis (a number of software do that very nicely!) in order for the reader to access the data values. Just one example of how hard it is to read data from the graphs: for pH, quoted in the graph legend of Fig. 3: $pH = 7.175 + DpH/300$!! Hard to recalculate individual pH values without a calculator! Please add multiple axis and change symbol size and shape.

A new version of Figure 3 and 4 is proposed that follow the reviewer's recommendations (see new Figures).

2- Too much generalities: The paper contains a large number of general sections with Figures and equations which are long and probably unnecessary. Especially, section 2.3.1 "Identification of biogeochemical processes...", is too long, verbious and not so clear. It is more textbook matter when presenting mixing models (lines 110 to 120 including equations 1 and 2 and Fig 1). I would consider shortening this part especially regarding the fact that "in situ transformations" are ultimately replaced by "transfer from the sediment".

Section 2.3.1 has been rewritten, including the suppression of ll110-120 and Figures 1 and 2. It has not been reduced in length since additional more detailed argumentation is now provided.

3- Treatment of error for ΔDIC_{ex} and ΔTA_{ex} : I understand that the uncertainty on the measurements of TA and DIC is very small (1 permil), and I acknowledge that. But I question the error calculation (and propagation) of ΔDIC_{ex} and ΔTA_{ex} . As it is written in the paper, these numbers are differences between the measured values (assume an infinitely small uncertainty) and the mixing curve defined by the end members. The authors quote an uncertainty on the mixing slope of 5% (see also Su et al., 2021). Hence the uncertainty on the difference of concentration ($DIC_{obs} - DIC_{mix}$) used for calculating ΔDIC_{ex} and ΔTA_{ex} would also be 5% of the DIC or TA at the salinity of the water mass (i.e. about $0.05 * 2000 \mu M = 100 \mu M$). This rapid calculation shows that the error on ΔDIC_{ex} and ΔTA_{ex} could be very large compared to reported values (100-300 μM Fig. 3). The authors should spend more time to convince the reader that uncertainties are smaller than my simple calculation or that the observed patterns are statistically solid.

The reviewer calculates the uncertainty in a similar way the ΔDIC_{ex} is calculated between x_1 and x_2 ($\delta(x)$ being the uncertainty on x), i.e.

$$\delta(\Delta DIC_{ex}) = \delta(DIC_{ex}(x=x_2) - DIC_{ex}(x=x_1))$$

$$\delta(\Delta DIC_{ex}) = \delta(DIC_{obs}(x=x_2) - DIC_{mix}(x=x_2) - DIC_{obs}(x=x_1) + DIC_{mix}(x=x_1))$$

$$\delta(\Delta DIC_{ex}) = \delta(DIC_{obs}(x=x_2)) + \delta(DIC_{mix}(x=x_2)) + \delta(DIC_{obs}(x=x_1)) + \delta(DIC_{mix}(x=x_1))$$

With $\delta(DIC_{obs}) \sim 0$ and $\delta(DIC_{mix}) \sim 100 \mu M$ it comes

$$\delta(\Delta DIC_{ex}) \sim 200 \mu M$$

thus $\delta(\Delta DIC_{ex})/\Delta DIC_{ex} \sim 100\% !!$

However, this approach does not take into account the fact that the error on the slope would be the same for $DIC_{mix}(x=x_2)$ and $DIC_{mix}(x=x_1)$ and the difference between these two values cancel most of the uncertainty associated to the slope of the mixing line. The reason is that the difference of salinity between x_1 and x_2 is much lower than the sum of the salinity of x_1 and x_2 . Thus, we have much less uncertainty on

$\Delta\text{DIC}_{\text{ex}}$ (that is about 5% see below) than on DIC_{ex} (that is about 50%). It can be demonstrated by considering the relation

$\Delta\text{DIC}_{\text{ex}} = \Delta\text{DIC} - \text{sml_DIC} \times \Delta\text{S}$, there we have

$$\delta(\Delta\text{DIC}_{\text{ex}}) = \delta(\text{DIC}_{\text{obs}}(x=x_2)) + \delta(\text{DIC}_{\text{obs}}(x=x_1)) + \delta(\text{sml_DIC} \times \Delta\text{S})$$

With $\delta(\text{DIC}_{\text{obs}}) \sim 0$ it comes

$$\delta(\Delta\text{DIC}_{\text{ex}})/\Delta\text{DIC}_{\text{ex}} = \delta(\text{sml_DIC})/\text{sml_DIC} + \delta(\Delta\text{S})/\Delta\text{S}$$

$$\delta(\Delta\text{DIC}_{\text{ex}})/\Delta\text{DIC}_{\text{ex}} = \delta(\text{sml_DIC})/\text{sml_DIC} = 5\%$$

We add a sentence to clarify this point to the reader (I154-156)

Posing $\delta(x)$ as the uncertainty on x , we get equation (6) that describes the fact that the uncertainty is much lower on $\Delta\text{DIC}_{\text{ex}}$ than on DIC_{ex} because most the error associated with the calculation of the endmember is cancelled when calculating the difference of DIC_{ex} on two points with close salinity:

4- Negative biogeochemical pathways: in several occasions (Table 2, line 1 and line 290 “primary production (-AR; Aerobic Respiration)”; line 365 “negative SR; Sulfate Reduction”), the authors provide shortcuts in biogeochemical reactions which are clearly wrong. Primary production process is definitely not the negative aerobic respiration except in some mass balance equation summarizing the effect of these processes on water chemistry. Same for sulphate reduction and sulphide oxidation. The biological organisms that conduct these transformations are different, the biochemical pathways are different. The authors should reconsider their way of presenting these biogeochemical processes.

We agree that the organisms' involved and biogeochemical pathway differs between forward and backward overall reactions. We add this precision to prevent any misunderstanding for the reader. Presentation of primary production is now (I.300): “primary production (whose overall mass balance equation is here summarized as negative AR)”

And lines 381-383:

“Combinations without MnR-MnC, however, lead to a negative SR whose overall equation could be interpreted as a possible small participation of anoxygenic phototrophic (purple) bacteria (Findlay et al., 2015, 2017) but are not considered further as the amount of $\Delta\text{TA}_{\text{ex}}$ involved would be tiny.”

5- Primary production in flood conditions: I think that the mass balance reaction and chemical ratio reaches its limits when the authors propose that primary production occurs during (or right after) the flood in 2018, and is counterbalanced by carbonate dissolution (line 306). It is known that turbid waters during floods prevent primary production because of light shading, and that primary production favours carbonate precipitation due to the removal of CO_2 and the increase of pH. Hence, even if the combination of CD-AR (Table 2, line 2) has the right chemical ratio ($\infty/0/-\infty$, line 306), it is very unlikely that these processes can occur in the turbid estuarine waters.

We recognise that simultaneous primary production with carbonate dissolution is counterintuitive since more frequent combination such as aerobic respiration with carbonate dissolution is more common and are also observed here (table2, line3). However, we measure an increase of oxygen and an increase of alkalinity with no DIC changes... which is also uncommon. Note that in the upper Chesapeake Bay, water pCO_2 is naturally high and is undersaturated with respect to CaCO_3 and that biological production did occur in areas of low turbulence and sufficient light penetration. Besides, an increase of Ca^{2+} is also observed simultaneously. We think

that the original manuscript takes enough caution to describe this feature (l. 318-321), and does not extend on this sensitive point:

“This original signature can be modelled by the combination of simultaneous carbonate dissolution (CD), the water column being undersaturated, and PP, in equal proportion (2nd line in Table 2); the carbonate dissolution buffers the DIC consumption by the PP.”

6- Line 373: The ratio of chemical elements observed in the sulfidic region are compatible with reactions involving MnOx and MnCO₃, yet the ratio of $\Delta\text{DIC}_{\text{ex}}/\Delta\text{H}_2\text{S}$ in 2017 and 2018 are not shown in a Figure to ascertain this point. It could be added in Fig.5 on a fourth panel or in another Figure.

We agree with the reviewer and add an H₂S versus TA plot in the Figure 5d

7- Line 365: the authors declare that several combinations of reactions (5-6-7 of Table 2) may provide the identified $\Delta\text{Ta}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}/\Delta\text{H}_2\text{S}$ of 2.4/1/0 in the suboxic zone. They state that it is not possible to choose between these three reactions based on the above ratio of elements. One possible way to decipher between these combined pathways is the C/N ratio produced by the reaction as they are quite different for reaction 7 than for reaction 5 and 6. The authors should investigate that point.

Unfortunately, we did not measure the C/N ratio in organic matter during this campaign.

Review #2.2

I am reviewing this manuscript for the second time and feel that the authors have tried to incorporate the comments of both earlier reviews. The split into results and discussion helped to improve the manuscript and section 2.3.1 is a nice addition (but: see below). I feel that I am less critical on the manuscript than last time, but at the same time I am not yet on the point where I can recommend publication.

General comments

The introduction lacks a proper build-up. In the new section on anoxic environments, suddenly alkalinity is used without introducing its link to carbonate dynamics in the first paragraph. I also don't understand the use and discussion of 'charge transfer'; for example, when Fe and Mn oxides are used for OM decomposition, they still change alkalinity. Finally, this section contains quite some inaccurate formulations: e.g., metal oxides are not a pathway (L. 42) and are not always transformed into sulphur or carbonate species; they can also remain in dissolved form.

We agree with the reviewer and rewrite in depth the second section of the introduction

Section 2.3.1 is a nice addition to the manuscript but not easy to read. I like to think that I am mathematically inclined, but I still don't follow all the reasoning here. First, the explanation now uses a mixture of 'hypothetical species' C and D in the equations, and TA_{ex} and DIC_{ex} as examples in the text. However, for example C and D in Eq. 3 to 5 cannot directly be replaced with TA_{ex} and DIC_{ex}, as they cannot be part of a reaction equation. So I suggest that you clarify how C and D are linked to TA_{ex} and DIC_{ex}.

We change significantly the section 2.3.1 to answer to both reviewers' comments. In particular it is now precised that (I124-125)

"Equation (3) is also true for any linear combination of a solute with a conservative element such as the salinity, S, because $\alpha_S = 0$, hence:

$$\frac{d^2C + kS}{dx^2} = \frac{d^2C}{dx^2} + k \frac{d^2S}{dx^2} = \frac{d^2C}{dx^2}$$

and later (I.137-139)

"In this study, while $\Delta TA \neq \Delta DIC \neq 0$, the excess of TA (TA_{ex}) and the excess of DIC (DIC_{ex}) are calculated by linear combination with salinity to be equal to zero for the upstream and downstream endmembers reaching the condition $\Delta TA_{ex} = \Delta DIC_{ex} = 0$."

Second, I don't understand where the 0.1 in Eq. 6 is coming from.

The 0.1 in Eq (6) come from the addition of two uncertainties of 5% as precised in I 141-143:

"The oceanic endmember varies mainly with season (Cai et al., 2020) and a maximal change of 50 μM results in 5% uncertainty on the slope of the mixing line."

Third, I don't think that the bow and the set of spears are as different as you present them. In my view, the bow is simply representing how the relative weight of the various reactions that make up each spear may change as a function of salinity.

These expressions and the related explanation have been deleted in the new version

At the same time, each of the spears can still include an additional source (e.g. from sediments or lateral exchange) and you seem to ignore this possibility in your calculation of v and v_i in Eq. 9 (L.167). When looking back at the comments on the earlier version, I see that this has also been pointed out then.

It is now clearly precise that the absence of a third endmember, or of significant lateral mixing is necessary to apply the “reaction driven” approach (I163-166)

“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 TA_{ex} versus DIC_{ex} as a sum of biogeochemical reactions spread all over the water column that can be broken into several discrete reaction zones.”

The final part of the discussion becomes very confusing (L. 404-419). How can you use a reaction driven approach if you explicitly state here that external inputs from the sediments are required? This seems very contradictory. It is only possible if 1) you include sediments as part of your system, which doesn't seem to be the case; and 2) extend the timescale, but then the steady-state assumption doesn't hold anymore. This point really needs clarification, and in fact probably means that the distinction between bow and set of spears cannot be drawn as black-and-white as this manuscript does.

We agree with both reviewer that this point needed to be clarified. Section 2.3.1 has been rewritten to fine-tune the demonstration introducing the concept of *local endmember* to explain steep changes of DIC/TA slope (see answer to reviewer #1).

We also tried to fluidize the explanation in the first section of 4.5 (I422-430):

This mass budget discrepancy cannot be solved invoking suspended material since the 88 μM of MnO_2 would require a suspended material concentration of about 4.4 g L^{-1} (assuming an average concentration of 20 $\mu\text{mol g}^{-1}$ of Mn), 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 (Cerco et al., 2013). However, a fast settling rate could satisfy and explain the discrepancy between water and solid concentration. But another process dephasing aqueous from solid reaction products is also possible at station 858, since the dissolved phase could have moved up, rather than the particles settling down. In this case, the SR-SMnC reaction was not happening only in the water column of the Chesapeake Bay and part of the TA_{ex} and DIC_{ex} pool could have been produced in the sediment during the previous year, then diffused out of the sediment simultaneously with other reduced elements as the summer begins.

A specific section has also been written (I444-452):

The assumptions detailed in section 4.1 permit the “reaction driven” approach to be reconsidered in regard to this sediment efflux scenario. Indeed, the sediment efflux does not need to be considered as an additional endmember, that would violate the third assumption, since its salinity and the pore water concentrations results from the upstream and oceanic endmembers superimposed to geochemical reactions. In section 2.3.1, we point out that equation (4) was valid in between each local endmembers and that the straight lines on the $\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}$ plot between them indicates that the local endmembers are maintained in steady state by a chemical reaction with a similar stoichiometry. These results indicate that even if most of the MnCO_3 was produced when the local endmembers were localised in the sediment, a- their migration does not alter the TA_{ex}/DIC_{ex} signature and b- the chemical reaction

that produced them is still ongoing at sufficient rate to maintain a steady state characterised by the steep changes of direction observed in Fig. 4a.

Detailed comments per line

L. 75–92: This section is very detailed in its experimental description but it lacks clarity on which Mn and Fe species are actually measured. I was only able to deduce this information from the results.

We add these information (l. 84-85):

Iron was measured on both bulk and filtered samples using the ferrozine method (Stookey, 1970): after HCl acidification (for Fe(II)) and an optional reduction step (for Fe(III)+Fe(II))

L. 102-103: I found this difference between the 2017 and 2018 campaigns quite interesting. Can you link it to the higher inflow of 2018 making e.g. the used equilibrium constants less reliable?

In some point yes. I think the relation is mostly conduct by nitrate and nitrite concentration: a) in 2017, the non-carbonated-TA find its minimum at the maximum of nitrite and b) the higher NO_2^- concentration in 2017 correspond to the lower non-carbonated-TA. The NO_3^- dataset is lacking, but the higher runoff in 2018 could have diluted the fertilizers...

L. 110-112: This is a very complex sentence. Please try to simplify.

L. 115-116: Also Eq. 1 is not valuable in case of such a change.

Figure 1 caption: not sure what you mean by 'a segment' here.

L. 126: Why not visually add this excess to Fig 1 in order to try to link C and D better with TAex and DICex?

The section of concern for the 4 previous comments has been removed

L. 130: "has to be determined" I would say that this is your choice and I would be really curious to know how much μM this TA endmember would have to change in order to add 5% uncertainty on the slope of the mixing line (as you discuss for the oceanic endmember).

We add the sentence (l. 145-146)

Between the two campaigns, the upstream endmember changed by $77 \mu\text{M}$ generating 5% of change on the slope (see Fig. A1).

Your previous manuscript version had a big discussion on the upstream endmember and although I understand your current choice, I would like to substantiate a bit more that it is 'less sensitive to short-term changes' (L. 133)

We precised the sentence (l 148-150):

However, it corresponds to a larger water mass pool, less sensitive to short term changes, with a residence time being higher than 240 days in the Chesapeake upstream part (Du and Shen, 2016), and thus is more likely to satisfy the condition of stability of the endmember, which is a prerequisite of the steady state assumption.

L. 140: Here you should use "net stoichiometry" (or "apparent stoichiometry" as you use later in this section), it is still a mixture of several reactions.

We add the adjective

L. 142-143: I'm not an expert in error propagation, but shouldn't the uncertainty be equal to the square root of the sum of squared uncertainties?

The square root of the sum of squared uncertainties is often used for analytical error propagation but will be inferior of the sum of uncertainties we are using. So, for sake of simplicity, we prefer to keep the equation unchanged

L. 147-149: I don't understand this sentence, Eq.6 doesn't describe a single solute. Shouldn't this refer to Eq. 4 instead?

True, we change the equation

L. 150: I don't understand this steady state assumption in the context of what you state in L.146-147 on the temporal evolution of water masses. Is this because you exclude additional sources from your model? (See comment above on spears versus bow)

This sentence has been removed in the new version of the section 2.3.1

L. 177: I feel that Eq. 12 needs a bit more credit to the earlier approaches linking charge with alkalinity than a short mention in L. 186-187 alone.

We add the equation 32 from Wolf-Gladrow et al. 2007 for comparison (l.195-199): Eq. (10) is equivalent to those published in Soetaert et al. (2007) or Wolf-Gladrow et al. (2007) whose equation 32 can be refined considering that :

$$\sum_i z_i^{pH=4.5} = [\text{Na}^+] + 2 [\text{Mg}^{2+}] + 2 [\text{Ca}^{2+}] + [\text{K}^+] + 2 [\text{Sr}^{2+}] + \dots$$

– $[\text{Cl}^-] - [\text{Br}^-] - [\text{NO}_3^-] - \dots$ TPO4 + TNH3 – 2TSO4
– THF – THNO2 – ...

However, Eq. (10) is more general. For example, in suboxic water, specific species such as polysulfides (as HS_8^{2-} , Rickard and Luther, 2007) and in highly productive environments, carboxylic groups from DOC can be easily added as soon as the bearing charges at pH = 4.5 are known.

L. 196: Similar zonation yes, but the 2018 profile appears noisier and the transition somewhat shallower (at 5-6 m depth rather than ~7m depth in 2017)

Yes, it is also one of the reason why plot against salinity is preferred farther.

L. 199-203: This is again a very complex sentence. You write about pCO₂ lower than atmospheric but then mention values of 505 and 770 uatm? I don't follow this.

We clarify this sentence, indeed the average on the zone considered are above atmospheric value but some sample show lower pCO₂ (l. 209-214).

Below, at 3 m depth, a subsurface layer (named primary production zone or PP in Fig. 2) is characterized by a high amount of O₂ (about or above 100% saturation), high pH (about 8; 8.11 ± 0.07 , n=13 in 2017 and 7.94 ± 0.08 , n=14 in 2018) and high day to day temperature variation (above 1 °C between different days). The layer presents relatively low pCO₂ ($505 \pm 75 \mu\text{atm}$, n=13 in 2017 and $770 \pm 130 \mu\text{atm}$, n=14 in 2018) with minimal values at 110 μatm in 2017 and 205 μatm in 2018, which are below the atmospheric pCO₂ of 407 μatm (Chen et al., 2020)).

L. 212: I don't like the term 'suboxic' anyway (I prefer hypoxic; in fact your ILO zone can be called hypoxic zone) but $<1 \mu\text{M}$ already is anoxic.

We didn't call "hypoxic" the ILO zone as some scientists will not like that an hypoxic zone with $105 \mu\text{M}$ of O_2 .

Anoxic and euxinic/sulphidic have clear different meanings (anoxic meaning without oxygen, euxinic meaning free sulphide present), so using anoxic here is more correct. Then, in L. 223, you can write "the transition from sulphidic to anoxic zone" which also seems more correct.

Anoxic and euxinic/sulphidic have clear different meanings but a sulphidic water can be anoxic too, which can lead to misunderstanding. By the way, some sulphidic water can have also oxygen since reduction of oxygen by free sulphide is rather slow... we add the precision l.223-224 and change the zone name from suboxic to anoxic:

Deeper, where the oxygen is not detectable ($< \sim 1 \mu\text{M}$) and in absence of free sulphide, the so-called anoxic zone ...

L.241: I'm not sure if you can deduce from Fig 3 and 4 that the stratification is similar. In fact that is more clearly shown in Fig. 1. Maybe a different wording would better fit what you want to describe here (e.g. zonation?)

We change "stratification" by "zonation"

L. 249: A zone with neither oxygen nor sulphide present is an anoxic zone, not a suboxic zone. See my earlier comment on this topic.

L. 264-266: As said before, I don't think this is "either/or". It might be more valid to say that one dominates the other (i.e. reactions dominate over mixing, in this case).

We suppress the sentence, and added the concept of domination in the following sentence (l.275-278)

At station 858, the steep gradient observed, for example the pH and pCO_2 gradients in the PP zone, the O_2 and NO_2^- gradients above the anoxic zone and the Mn, Fe and H_2S gradients at depth, suggest that ongoing in situ processes control the changes of concentrations and dominate the time-dependent endmember variability or the mixing with an unknown third endmember.

L. 274-278: This is quite a list of assumptions – good that they are explicitly mentioned. I don't understand the difference between #2 and #3 – what do you mean with 'starting point'? If that is in time, it is similar to a steady state, isn't it?

We agree with the reviewer and modify this sentence as (l.283-287):

Assuming 1) that mixing is efficiently described by vertical turbulent diffusion mixing, 2) that the measured concentrations correspond to a steady state – no changes observed over the 1 week sampling, 3) that no additional endmember contributes significantly to the excess calculation, in particular that the samples are isolated from atmospheric exchanges and 4) that lateral mixing is negligible, which is equivalent to the lateral invariance of the system – as in the stratified water column of station 858;

L. 282: "this interpretation does not identify reactions with minor impact on the carbonate cycle"- because of a low rate, or their stoichiometry, or both?

Because the product of rate x stoichiometry is too low compared to other reactions. We add a reference to the equation (7)

$$\alpha_c = \frac{1}{v} \sum_i \alpha_c^i v^i$$

L. 292: “which corresponds to the occurrence of only net aerobic respiration (AR)” – two comments: 1) add this indicates that $AR > -AR$ (you use the same symbol for AR and net AR now),

we add the precision (I.304-305)

Note a - that “net aerobic respiration” indicates that primary production is possible at a significant rate, but slower than AR;

and 2) given that the slope is 0.1 and ΔTA of AR is 0.15, something else must have occurred with alkalinity as well, unless you have clear indications that OM was very different from Redfield ratio. If you were to fit ΔTA rather than ΔAOU , you would probably have around 15-20% of the produced NH_4^+ nitrified, I guess? What would then be the resulting ΔAOU ? Are there indications that it's more appropriate to fit ΔAOU rather than ΔTA ?

Since AR only fit rather well the dataset (Occam's razor), we didn't investigate further. However, we recognise that the fit to ΔTA gives very interesting value. We modify the Table 2 accordingly and add the sentence (I.307-308)

A combination of 1 AR and 0.025 Nit (nitrification of 16% of the produced NH_3) improves the modelled value to 0.1/1/1.05.

L. 306: I don't understand the infinity symbols here. Yes, $\Delta DIC_{ex} = 0$ but since you compare the slopes of three different species, $\Delta TA_{ex}/\Delta AOU$ will not equal infinity. Otherwise, you have to present $\Delta TA_{ex}/\Delta DIC_{ex}/\Delta AOU$ differently and make it clear that you always compare $\Delta TA_{ex}/\Delta DIC_{ex}$ and $\Delta AOU/\Delta DIC_{ex}$, as you do in Fig 5 and Table 2. But from the way it is in the text, and also because you fit three reactions to three equations, this isn't obvious at all. The same applies to the presentation of $\Delta TA_{ex}/\Delta DIC_{ex}/\Delta H_2S$ later on.

The signature has been calculated and added in the text (I.317-321).

In Fig. 4a and 4b, this process translates into a vertical distribution at $DIC_{ex} = 40 \mu M$ with $\Delta TA_{ex}/\Delta DIC_{ex}/\Delta AOU = 1.37/0/-1$. This original signature can be modelled by the combination of simultaneous carbonate dissolution (CD), the water column being undersaturated, and PP, in equal proportion (2nd line in Table 2); the carbonate dissolution buffers the DIC consumption by the PP. Note that the ratio between $\Delta TA_{ex}/\Delta AOU$ implicates significant nitrification.

And later (I.334-335)

Additionally, in 2017 the $\Delta TA_{ex}/\Delta DIC_{ex}/\Delta AOU$ system indicates weak nitrification, while in 2018 significant nitrification in the ILO and PP zones are suggested by the “reaction driven” approximation.

L. 314-322: Why would nitrification occur in this zone in 2018, but not in 2017 or in the zone above? The reasons regarding kinetics (L.296) prevail here as well. Are there logical reasons to assume that kinetics are limiting above (where O_2 is higher), but not in this zone?

We add an addition hypothesis concerning this point I.335-338

The role of nitrification in explaining TA_{ex} depletion is only hypothetical since no direct measurement of NH_4^+ and NO_3^- were not performed. In particular, TA_{ex}

depletion is particularly intense during high flow, high suspended particles season and could be produced by NH_4^+ adsorption to the particles rather than by nitrification.

L. 327-329: Well, that depends on what you want to know. I am not sure if I agree; it depends on whether the combined $\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}/\Delta\text{H}_2\text{S}$ can be derived by multiple combinations of multiple processes.

We precise “to fit with the “reaction driven” interpretation”

L. 336-344: reading this makes the focus on charge in the introduction much more understandable. I would move this text to the introduction and merge with the current paragraph (still taking into accounts the comments).

The concepts of “charge transfert” has been removed from the introduction

L. 345-347: But you measured these species, didn't you? Why don't you make this decision based on your measurements, such that you can substantiate this choice? When looking at your measurements, I am not sure if your measurements substantiate this choice; especially given that you discuss their dynamics in the result section as well.

We add the precision (l.363-365)

These species are usually recycled rapidly and hold a role of catalyser or electron shuttle between other redox species and did not reach $10 \mu\text{M}$ during the campaigns (Fig. 3).

L. 351-353: I don't know what you want to achieve by including this reason, but the fact that you cannot distinguish SR followed by H_2S oxidation from AR in your model, does not mean at all that this set of processes isn't important. It just means that you cannot conclude it from your model.

Yes, we add the precision (l. 370-372)

As an example, the chemical equation of SR followed by H_2S oxidation with oxygen is equal to the equation of aerobic respiration: the proposed model confounds both pathways because the resulting chemical changes are similar.

L. 359: “as the only Fe product is FeS or FeS_2 ”- where? In your model or in reality? (i.e. as can be deduced from your measurements)

We now precise (l.377-379)

Direct respiration of FeOOH is also taken into account, but as the only final Fe product in the model is FeS or FeS_2 , it has to be accompanied by some SR (FeSR - FeS).

L. 363-368: I find this section much more strongly formulated than L.360-362 which, in itself, leads to speculation. So I would revert the order: any reaction in combination with MnR - MnC leads to the production of the ratio, and some of them are more likely than others.

We follow the reviewer recommendation and suppress the lines 360-362

L. 370-372: Measured concentration of MnOx are quite low; are they high enough to support this statement?

This point is investigated in section 4.5

L. 372-374: This is quite short; which set is the most likely? Do you expect this to be

the same set as in the anoxic zone? It the same set that in the anoxic zone, but part of the H₂S produced has not been oxidized yet.

And what about sedimentary input? (which you discuss earlier that it must be an important source) Again this comes back to the lack of external inputs into your reaction-driven model.

We clarify this point rewriting these sentences (l. 389-394)

Deeper, the vertical gradient of sulphide suggests that part of the H₂S came by diffusion from the sediment's porewater (Fig. 2). The assumptions required for the "reaction driven" approximation are still valid as soon as steady state is maintained by ongoing reactions, even if one of the local endmembers has not been sampled since it is probably located in the sediment. In the presence of sulphide, the $\Delta TA_{ex}/\Delta DIC_{ex}/\Delta H_2S$ signature is 2.4/1/1.2 in 2017 and 2.4/1/3.2 in 2018 (Fig. 4a and 4d) and can be explained by the same combination of reactions without complete oxidation of H₂S from SR to take into account the build-up of H₂S (Table 2).

Table 3: Aren't there studies from the Baltic Sea water column that you could include here? That system may be more similar to the Chesapeake Bay water column than many of the other systems discussed in this table.

Most of the Baltic Sea water column dataset we found was

Kulinski et al., 2014 whose dataset come from surface water with no indication about the oxygen concentration

And Beldowski et al. 2010 whose dataset encompass both oxic, anoxic and sulphidic water column. However, data was not available (at least rapidly) and would require an extensive data processing to identify the different endmembers (up to 5 are defined in the publication) and calculate the corresponding excess of TA_{ex} and DIC_{ex} (DIC_{ex} has been already calculated) which is beyond the scope of our study.

L. 398: "The rhodocrosite saturation (Luo and Millero, 2003) is always below 0.3" – where? In the Chesapeake Bay?

We add the precision "in our samples"

L. 399-401: So this boils down to my earlier comment – a reality check on your model results.

L. 404-419: Here I get really confused – see general comment.

L. 420-426: This upscaling seems a bit out of place, given that the Chesapeake Bay may not be representative at the global scale. This is in fact the main conclusion of your study, that you show the exceptional $\Delta TA_{ex}/\Delta DIC_{ex}$ ratio. I would therefore suggest to remove it. We follow reviewers' comment and remove this section

L. 436-439: These lines seem out of place in the conclusions, also in the context of my previous comment. We write again the conclusion, removing the reference to charge transfer concept.

Figure A3: What is meant with the "dMnT..." comments for Cast #10 of 2017? We modify the figure to make it clearer

Technical comments

General: especially the newly written sections contain many typos and sloppy writing.

I did not identify all occurrences but highlighted a few below.

L. 12 (and many more occurrences): use 'dynamics', not 'dynamic'

L. 12: 'carbonate minerals'

L. 39: 'anoxic environments' (reactions are anaerobic)

L. 56: 'a single station' sounds better in my opinion

L. 168: "reaction stoichiometry"

L. 175: "species"

L. 198: Explicitly refer to Fig. 3 here.

L. 209-215: add (n=xx) in between brackets for clarity. Also this text is complex to read.

We gratefully thanks the reviewer for these typos correction that have all been taken into account