



EGUsphere, author comment AC1
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Reply on RC1

Aubin Thibault de Chanvalon et al.

Author comment on "Influences 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-AC1>, 2022

Reviewer #1 did an intensive reading of the document resulting in important general comments supported by many detailed criticisms. Reserving our detailed answers for the final response, we would like to address here 3 of the main comments made by Reviewer #1.

First, Reviewer #1 was frustrated by the presentation of the data. In particular, he/she suggests that Figure 1 aggregates two sampling periods, longitudinal gradient along the estuary and vertical gradients. This frustration is indicated often, sometimes by requiring a map to describe clearly the longitudinal gradient, sometimes requiring vertical profiles with depth in the y-axes. It seems that all this frustration came from a misunderstanding, that could easily be avoided if the manuscript does a better job underlining the sampling design. However, in the current manuscript it is indicated precisely that "During two sampling campaigns from August 3rd to 9th, 2017 and July 28th to August 3rd 2018 eleven profile casts were conducted in a 25 m water depth in the Chesapeake Bay (Station 858, 38°58.54'N; 076°22.22'W)". This text indicates that all the samples came from the same location, reducing considerably the interest for a map and the pertinence of the reviewer's criticism about longitudinal variations. Additionally, the Figure 1 clearly separates the 2017 campaign from the 2018 campaign avoiding any confusion. Finally, the reviewer suggests that plotting data against depth will better describe the vertical gradient than plotting data against salinity. Density plots (here approximated by the salinity) are often preferred to depth plots and in our case makes the data from the same time period much more comparable.

Second, about the science, the criticisms made by reviewer #1 are more fundamental. The current manuscript fails to convince him/her about the rationality of the method and about the strength of the conclusion. Our goal is to investigate the influence of iron and manganese on alkalinity (TA). Important variables such as dissolved inorganic carbon (DIC) and apparent oxygen uptake (AOU) are also reported. The method has two steps, first we identify all the processes likely to modify these 3 parameters based on our understanding of the environment. Second, we combine these processes, with different intensity, to get a model fitting the data. Among the combinations that fit, the simplest one (with less involved processes) is preferred (Okham razor). Reviewer #1 regrets we don't estimate the CO₂ invasion in the water although it certainly happens. It will be done, but it was neither the goal of the manuscript nor requested by the method since parameters in the most superficial layer are fully explained based on 1 process: aerobic respiration. It is not possible to assess the relative importance of each potential process,

we only identify the preponderant one. The variations of CO₂ invasion impact with depth are probably too small to compare to the variation of respiration impact on the ratios TA/DIC and TA/AOU.

Finally, the main criticism by Reviewer #1 is *"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)..."* Note that this important reactivity of MnOx and Mn(II) was observed during both campaigns.

"... 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..."

Mixing, and mixing intensity (between waters) will not directly modify the DIC_{ex} or TA_{ex} because they are conservative during mixing. It is the reason why we are using them (for example pH is not conservative and does not support the discussion). Only reactions can modify this ratio. Mixing plays a role only if it favours rapprochement followed by reaction between two species. That is why our approach (Table 1) – and it is part of the originality of our ms - takes into account sequences of reactions that can occur in a water mass from its equilibrium with the atmosphere to the position where we sample it. About the importance of reactions intensities: the DIC_{ex}/TA_{ex} produced by one reaction is independent of its intensity which is one other strength of our approach. In case of many simultaneous reactions, the relative intensity is important and is taken into account in our approach. For example, the $\Delta\text{TA}_{\text{ex}}/\Delta\text{DIC}_{\text{ex}}$ of 0.77 associated with a $\Delta\text{DIC}_{\text{ex}}/\Delta\text{AOU}$ of 1.5 can be fitted by the combination of 1 mole of organic matter respiration simultaneously to 0.5 mole of carbonate dissolution (Table 2).

"...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."

When we describe a sequence of primary reactions followed by any secondary reaction such as CaMn precipitation we surely take into account the effect of secondary reaction, as this is the goal of building these combinations. That is why we speak about *net* reaction and take into account only species available in large quantities likely to react from its equilibrium with the atmosphere to the position where we sample it. No intermediate species produced after atmospheric equilibrium and consumed before sampling such as catalysts are relevant in our approach. That is why the reviewer's comment *"If H₂S is totally reoxidized by O₂, then the overall delta TA is null."* is not relevant: the overall delta TA needs to be considered from the equilibrium of the water with the atmosphere. Therefore, the reaction producing H₂S has to be taken into account, namely sulfate reduction, to generate an overall delta TA of 0.15 (produced by nutrient release) as illustrated by the reaction SR-O (Table 1).

Some of the discussion provided here can surely be added in the discussion section for clarification. However, we demonstrate that the main criticisms from reviewer #1 do not break down our demonstration that only a reaction producing metal carbonate is able to generate the observed TA/DIC ratio of 2.4.