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

The paper 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 (MnCO3), 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 MnCO3. 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.

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 haow 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.

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".

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 (DICobs-DICmix) 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*2000µM = 100µM). This rapid calculation shows that the error on ΔDIC_{ex} and ΔTA_{ex} could be very large

compared to reported values (100-300µM 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.

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.

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 (∞/0/-∞, line 306), it is very unlikely that these processes can occur in the turbid estuarine waters.

6- Line 373: The ratio of chemical elements observed in the sulfidic region are compatible with reactions involving MnOx and $MnCO_3$, yet the ratio of $\Delta DICex/\Delta H_2S$ 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.

7- Line 365: the authors declare that several combinations of reactions (5-6-7 of Table 2) may provide the identified $\Delta Taex/\Delta DICex/\Delta H_2S$ 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.