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 $\Delta TAex$ to $\Delta DICex$ 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 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.

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.

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. 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.

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.

L. 19: What do $\Delta DICex$ and $\Delta TAex$ mean? Better not to use these abbreviations in the abstract.

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%.

L. 31: "shallow waters"

L. 32: "carbonate dynamics"

L. 39: not sure why specifically HCO_3^- dynamics is used here. Isn't this more generically carbonate system dynamics?

L. 48: "sampling campaigns" (I stopped identifying typos here as there are too many)

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).

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

L. 91-92: Which CRMs?

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.

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?

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

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.

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

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.

L. 152: "the processes" – which ones?

L. 152: "overall much lower salinity". Maximum values declined from ~20 to ~16, I wouldn't call that 'much lower'

L. 155: atmospheric pCO2 was likely higher than 400 uatm.

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

Fig. 1: I am not sure how correct it is to use a linear transformation for plotting for a non-linear variable like pH

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?

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+.

L. 184: "emerging picture"

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

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.

L. 216: "as was observed for other years" – including 2017 or not?

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) Also, are any analyses done on the type of algae that would contribute to PP?

L. 237: "never reported in the literature" – perhaps in estuaries or using this particular metric or ΔTAex/ΔDICex (although I am not even certain about this). But ratios of TA/DIC exceeding 2 have been discussed in earlier works.

L. 252 – 258: My main issue with this discussion is that there can be more fates of H2S than only discussed here, each having a different ΔTA/ΔDIC 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 and since solid S species or MnCO3 have not been measured. As a result, the authors cannot state whether the formation of MnCO3 is actually important in the Chesapeake Bay. In fact, the authors state this to some extent themselves in L. 269-270.

L. 279: I don't understand the unit of ΔTAex here – or is something else meant?

L. 229 – 330: see comment before – I am not sure if this is really the case.