Reviewer 2 Response

(*Reviewer Comments*, Response, Proposed Changes)

1. *I must admit that I am conflicted in making a recommendation of this paper. First, this is my favorite subject and I like the approach of a combination of data and modeling (also a combination of numerical model and simple mixing model). However I do not think the combination is successful … If the authors can address these serious issues reasonably, I feel this paper can be a good contribution to our field. Here are my suggestions … if the numerical model study of the Fraser case is new (say it), perhaps expand the model description and limit your discussion to this case, which is essentially what you did but just don't call it global extrapolation.*

   We appreciate the detailed feedback provided by yourself, the other reviewer and the editor, and would enjoy the opportunity to revise the manuscript in accordance. We agree that we have extended some of our analyses beyond their scope and in doing so have unwittingly lost focus in the manuscript. We propose that we scale back to focus our analyses only on the Fraser River. We will still place it in the context of other global rivers (Figure 6) however we will remove the end-member analysis that relied on DIC and TA from other world rivers (Figures 5-d and 7).

   Specifically, we will provide additional detail concerning the Fraser and its estuary, including what is known and less known regarding the drivers of the inorganic carbon cycle. The river is a key driver and yet we have few reliable carbon data in the fresh and brackish waters in the study region. This paucity provides a strong motivation for our analysis. By clarifying this motivation in the text, the key results will be highlighted. We will include the additional references (not all of which were available at the time that this manuscript was submitted) that the reviewers have suggested, where appropriate. We also will define new sensitivity scenarios to include more recent and newly acquired data where possible and reduce (and sometimes remove) the dependence on data in which we have less confidence (such as data collected using outdated methods or river TA with high organic alkalinity uncertainty). We will re-run all the simulations with these new scenarios and produce a new sensitivity summary figure (4), with clarified presentation, to reflect these new results. Finally, we will strengthen the delivery of our main findings and highlight the importance of using the biogeochemical coupled model by refocusing our results (3), discussion (4), and conclusion (5) sections to target the key points below.

   Key points

   (a) Responses of estuarine pH and Ω_A to Fraser River DIC-TA are asynchronous and strongest at opposite ends of the Fraser DIC:TA range.

   (b) Seasonal estuarine productivity reduces estuarine pH sensitivity to river chemistry during summer

   (c) Future Fraser River flow regimes with lower flow in the biologically productive season will favor lower estuarine pH and Ω_A, but the river will dominate a smaller areal region in the estuary.

2. *… the paper doesn't present much new data. I believe most new data and the numerical model were published in their two earlier publications (authors really need*

to say what is new here).

We appreciate reviewer 2's comment and will revise to clearly lay-out the novelty of this study. This study examines the response of near-surface DIC:TA, pH and aragonite saturation state in our 1-D model (presented originally in Moore-Maley 2016 - detailing model evaluation and basic results/drivers for a *single* river chemistry) across more than 200 year-long runs with different river chemistry scenarios. The results of these runs with varied river chemistry are not published elsewhere. (The run parameters were chosen to simulate our best understanding of seasonal Fraser River DIC and TA, based on previously published total alkalinity observations in and around the river delta, an unpublished mooring pH timeseries in the river delta and finally, limited data mostly with S $>$ 20 from the Fraser estuary - which were published in Ianson et al. 2016.) We will add some more recent new unpublished data from the Fraser estuary (single campaigns in 2014, 2016 and 2017) to further inform new sensitivity scenarios. These data will be highlighted.

We will also shorten and de-emphasize the data methods section (2.2) and move our discussion of organic alkalinity to the study area description (2.1) to clarify that this is a modelling study. We will also scale back our data description in the last paragraph of the introduction to allow the modelling objectives stated there appear more clearly to the reader.

3. *... the first sentence in the beginning of the Discussion (p.8, line 18-20) says: "To conceptualize why model estuarine pH is lowest at high TA_f" ... this statement is only true in the situation the authors created that is the ratio of river DIC:TA = 1.02 to 1.1 ... it is not "high TA_f" but a high (DIC-TA) or DIC:TA in river water that is important here and is the reason behind the phenomenon ... I refer the authors to the paper by Liang et al. 2017 ...*

   We agree with the interpretation of reviewer 2 here that the changes in the freshwater DIC-TA (at constant DIC:TA ratio) are responsible for the pH vs S differences between the low and high freshwater TA cases. We also acknowledge that we refer to freshwater TA changes throughout this manuscript without mentioning DIC, which is misleading since we are always in fact manipulating either freshwater DIC:TA or freshwater DIC-TA or both. We will clarify our discussion of river TA scenarios in terms of DIC:TA and DIC-TA.

4. *... in extrapolation of the results, the authors didn't consider temperature effect but this effect can also be significant in controlling carbonate system speciation.*

   We plan to limit the generalization of our results in other estuaries and remove Figure 7 and the last 3 paragraphs of Section 4.2.

5. *If the examples cited by the authors are also true in the Fraser River (e.g., as high as 90% of TA is organic alk), then, how can we believe the DIC_f calculated from the pH_f and TA_f?*

   We based our freshwater TA endmembers on several data sources, some of which were collected in the Fraser River. By limiting our new endmember scenarios to data collected in the Strait of Georgia where we expect organic alkalinity contributions to be less significant, we can reduce the uncertainty in these scenarios. We will add more recent observations from the Strait of Georgia (see REVISION V above) and remove all TA data collected using outdated methods or in freshwater where organic alkalinity uncertainty is high.

6. *... the extrapolation of the Fraser River DIC:TA ratio globally is just not appropriate ... please fully assess the uncertainty of your assumptions. Here the assumption of* DIC_f*:*$TA_f > 1.02$ *probably not just changes the result slightly it perhaps will change the major conclusion derived.*

   We have decided to remove the extrapolation to global rivers including the last figure. We will only put the Fraser River in *context* of global rivers (Figure 6 in the original manuscript).

7. *... the paper is poorly prepared and hard to follow (see my detailed reading notes) ... the writing is not transparent to me. So a thorough rewrite with a better readability is also needed.*

   The paper will be thoroughly revised (see the "Outline" in our response to the Editor) and we will use your detailed reading notes.

8. *Fig. 4 is particularly hard to understand or guess.*

   The revision will include an additional figure with selected (model) timeseries from individual years. We will explain how we go from the time series to points on Figure 4 to clarify where this synopsis figure comes from (see point IX in our response to Editor). We will also clarify the text.

9. *... p.9, line 10, it says "This asynchrony arises because the response of estuarine carbonate ion over the large range of river* TA_f *and* pH_f *scenarios is more sensitive to changes in total DIC than shifts in the equilibrium point of the carbonate system." First, I don't understand what this sentence really says. Second, it sounds like to suggest that one can change all three parameters (*TA_f*,* pH_f *and* DIC_f*) at the same time. If here "DIC" is not river DIC but internal estuarine, biologically modified DIC, this is probably true, but the authors didnt say that.*

   We will clarify this sentence. The first phrase is confusing. Briefly, we wish to indicate that the concentration of the carbonate ion is more sensitive to the total amount of DIC (in the estuary) than the balance between the forms of DIC (which varies with pH). Your next point builds on this result.

10. *In the abstract (p.1, line 10), it says "rivers with high DIC and TA produce lower estuarine pH due to an increased estuarine DIC:TA ratio, but higher estuarine* Ω_A *because of DIC contributions to the carbonate ion." I like this statement. But I do not really see the result description and an extensive discussion of in the text body. Does this indicate that authors have changed mind a bit on exactly what they want to focus on in this this paper?*

    Thank you. As explained above we will refocus the paper. The difference between the response of pH and Ω_A is a key point and will be a focus in the revision.

11. *I do not like the implications for future climate. You have speculated too much! (To say high atmospheric* CO_2 *will increase river* pCO_2 *is simply wrong as river* pCO_2 *is generally so much higher than the atm-*pCO_2*.) So simplify it and merge it in the Discussion with just a few sentences.*

We will significantly rework our future climate implications section (again, please see the "Outline" in our response to Editor) so that it concerns only the Fraser river and clearly focuses on changes in the Fraser's hydrograph (decreasing freshet) that are anticipated with higher certainty. Potential changes in end-member chemistry will be discussed briefly and with care, clearly detailing the high uncertainty.

Reviewer 2 points out correctly that our text was misleading, and that many rivers are not likely to have increased DIC in future. Some fresh water end-members however may have increased DIC, as they tend to be at atmospheric equilibrium (e.g. glacial melt-water). As reviewer 2 knows, future DIC extrapolations also depend on the concurrent T change (a T increase could leave DIC unchanged even with increased pCO_2) leaving significant unknowns and low certainty.

12. *Finally your summary is too long and repeats too much of the Discussion.*

    The summary will be focused on the key points list above and we will ensure it is not repetitive.

13. *p.2, Line 15-16, Is this true? I have not seen a river whose TA is NOT flow-dependent. Perhaps, it is because the West paper is about the silicate weathering. Not sure if this is also true for carbonate weathering.*

    We did not intend to indicate that TA in other rivers is not flow-dependent. Our intent was rather to divide strongly flow-dependent from weakly flow dependent. We will rewrite this paragraph for clarity.

14. *p.4, line 15-18, Carbonate Alk is about 50% in the Satilla River Georgia (Cai et al. 1998). Again Cai et al. (1998) paper should be cited as it is the first study of this issue.*

    Noted. We will cite Cai et al. 1998 with respect to organic alkalinity in the new manuscript.

15. *p.4, Line 15-18, this really worries me. If TA data quality is so bad and the organic contribution is so large, how do we know the rest of modeling is correct?*

    We will add more recent discrete observations from the Fraser estuary (point 5 above) and remove all TA data collected using outdated (and even uncertain) methods or in freshwater where organic alkalinity uncertainty is high.

16. *p.6, Is RMSE = 0.16 pH unit a small uncertainty? It appears quite large to me. Perhaps you need to put it in the context of overall pH change.*

    Good point. We will add the range of pH and also calculate a Willmott score to show the model skill.

    Reviewer 2 is correct that variability in pH is indeed high in the estuary - the new figure with individual year timeseries traces will also add context for the reader.

17. *p.7, line 11 says "We define our three constant TA_f scenarios", then line 17 says "We define our three constant pH_f scenarios (Table 2)" (first there is no pH_f in Table 2). I am quite confused if these are related or separated assumptions? From my comment below on Fig. 5 caption, I don't think you need to call them "constant TA_f or pH_f", just river endmember scenario 1 to 6 is enough. They have nothing to do with whether TA_f is constant with river discharge; they are just your scenarios.*

We used a combination of scenarios: so 3 different pH_f and 6 different TA_f for a total of 18 different scenarios, hence 18 boxes on each plot in Table 4. We will completely restyle our presentation our analyses (see response to Editor - VIII) in terms of DIC/TA and DIC-TA and we will assign a run-number, as reviewer 2 suggests, to each model river chemistry scenario. Also, the scenarios themselves will be revised (Editor response – VII).

18. *p.7, line 20, I do not understand this: "Given the large seasonal temperature change (> 15 °C increase in summer), a constant pH_f implies a summer DIC_f decrease due to temperature (causing DIC_f:TA_f to decrease by about 0.06)". Why does increased temperature lead to DIC_f decrease? Is this just a decreased solubility effect or increased river pCO_2 leads to more CO_2 degassing? Do you mean that under constant pH_f and Alk_f, higher temperature leads to lower DIC_f? That is true. But the real question is what is really controlling the pH_f at constant TA_f but allowing DIC_f to decrease? You can't just set a certain parameter constant arbitrarily. Anyway you need to explain your assumption. Reading Fig. 5 caption (b), I finally see how you did it. You selected two TA_f values one low and one medium-high. Then at each TA_f, you selected three pH_f values and calculated 6 DIC_f values. Then you take these 6 TA_f and DIC_f combinations and mix them with the same seawater (TA_{sw} and DIC_{sw}) to generate the 6 mixing lines. I assume at least b and c should be based on these 6 same simulation. (For panel d, it seems you used the variable TA_f.) My question is: are these combinations realistic? I now take your 6 combinations and put them into CO2SYS (I assume $T = 15$ °C and all other acid = 0) and verified/confirmed your DIC_f and DIC_f:TA_f. No problem except that all DIC_f:TA_f ratio > 1.02. This doesn't make sense to me. Perhaps it is true for the low TA_f rivers (but in these river the org-ALK is often large), DIC:TA < 1 definitely occurs in medium and high TA rivers.*

    First, we are grateful to reviewer 2 for their meticulous consideration of our scenarios. Reviewer 2 is correct in that our intent was to indicate that *"... at constant pH_f and Alk_f, higher temperature leads to lower DIC_f according to CO2SYS"* however, it is clear that our original text was confusing. Our response above to #17 fully clarifies our previous scenarios and more importantly our plans to significantly revamp both the actual river chemistry scenarios and their presentation. (The mismatch in reviewer 2's CO2SYS results and our scenario is due to the fact that the actual T in the Fraser river and in our model is not static - varying from 4-20 °C during the year.)

19. *p.7, line 30-33, It is very hard to understand what the authors try to say after reading this part and Fig. 4 many times. Are DIC:TA (Fig. 4b) or pH (Fig. 4d) averaged over the estuary or what? Very frustrating.*

    Again we thank reviewer 2 for their careful review. The revision will include an additional figure with example time series (Editor - IX and response to #8 above). We will explain how we go from the timeseries to points on Figure 4 to clarify where this synopsis figure comes from. The new discussion of the individual traces will clarify the averaging.

20. *p.8, the description of Fig. 4 is not very clear. Figure 4 is not clearly labeled. Some supplement instructions are needed. (Like does all gray and white sections in figure*

4b, 4c, 4d mean different pH scenario? What does the "5 and 4" mean in figure 4f)?

A new revision will include an additional figure with example time series. We will explain how we go from the time series to points on Figure 4 to clarify where this synopsis figure comes from. We will complete the labelling.

21. *p.8, I am shocked that line 16 moves into Discussion. Now I realized that the entire ms is essentially a model study of pH sensitivity to river discharge and (DIC:TA)$_f$ ratio (the latter is also a function of discharge). Then, I went back to read their two earlier papers. The mode and the field data were already presented there. The authors need to say what is new of the first part of this paper comparing with the earlier papers.*

    We see that our original submission failed to put this new work in the context of the original model paper. See our detailed response to #2. Again, our previous papers focused on the estuarine carbon cycle as forced by physical and biological conditions in the estuary. However during that research it became clear that the river chemistry also had a substantial impact. This manuscript looks at that impact. All the model runs are new, as river chemistry was not varied in the previous model paper. We have also collected new data which will be included in the new manuscript.

22. *p.8, line 18-20, see main point.*

    Please see our response to the main point (1 above).

23. *p.8, line 28 to p.9, line 8, this is true. In the high river TA estuarine, DIC:TA is decreased slow whereas in low river TA estuarine water, DIC:TA is quickly modified and dominated by the seawater ratio. If this is the only point this paper wants to talk then why presenting the numerical model? Some of the other recent papers also talked about this point. However the assumption of same DIC:TA ratio for high* TA_f *and low* TA_f *rivers are likely problematic. Not sure how meaningful is this scenario simulation.*

    We are confident that a revision will clearly focus on our key points listed above and that our new scenarios and presentation will facilitate this focus. Also, our addition of model results (which are subject to the dynamics - sources/sinks within the estuary) to the figures presenting the theoretical mixing curves (see Editor response - X) will clearly show the utility of the numerical model.

24. *Page 9, Line 8: "Ocean pH and* Ω_A *are often assumed to be coupled": Some references may be needed here to support this. I think the word "coupled" and "decoupled" are misused here. In some sense, pH and omega are always coupled. They are just not "coupled" in a simple way as our "intuitions" may suggest. The simple case here is that* [Ca^{2+}] *increased as salinity increases, but that has no direct effect on pH. There are other more subtle factors or processes influencing pH and omega differently. However I do not think we can simply call that as "decoupled". You can find a better name.*

    Noted. In the new manuscript we will not use the word "coupled" but instead note that non-experts often assume lower pH implies lower Ω_A.

25. *p.9, line 12-14 is not clear.*

Noted. In the new manuscript we will expand and clarify as this is a key point of the paper.

26. *p. 10, I like the discussion on seasonality, but it is based on physics* (TA_f *and discharge only).*

    We will remove this section as we will focus on the Fraser River.

27. *p.10, line 14-16, true that high river* TA_f *systems like the Mississippi provide a strong buffer effect and its delta-pH shouldn't change as much as that in low* TA_f *systems during mixing. However biological production could raise pH to a very high value in the Mississippi.*

    Good point. The new manuscript will focus on the Fraser River.

28. *Fig. 6c and d, Note there are two arms of DIC:TA ratio to TA with a minimum at seawater TA. There is nothing magic here but the authors should mention the reason. The left reflects the mixing between the generally high ratio in river with a low ratio in seawater. The right arm reflects the mixing of a few very high TA rivers (with TA higher than the seawater) with seawater.*

    As we will focus the new manuscript on the Fraser River, we will remove Figure 6d.

29. *p.11, line 1 and 6 are not consistent. Warming allow more* CO_2 *degassing and decreases river DIC. Yes, I agree. But increased atmospheric* CO_2 *probably won't increase DIC as river DIC is so much higher than the atm-*pCO_2*. If there is any increase it likely increases TA equally (through increase of weathering rate).*

    In the new manuscript we will only consider the Fraser River and future climate changes we are sure about, for example, changes in timing of the freshet.

30. *p.10-11, I think this section is very speculative and should be deleted or combined into earlier discussion with short sentences. These speculations do not help, e.g., we do not know which competing factor will dominate and if river DIC will increase. Overall as the authors agree that these effects are rather small comparing with eutrophication induced surface biological production and subsurface respiration induced pH changes.*

    In the new manuscript we will only consider future climate changes we are sure about, for example, changes in timing of the freshet.

31. *p.11-12, I generally do not like long summary, which essentially does more repeating discussion.*

    The summary will be focused on the key points list above and we will ensure it is not repetitive.

32. *Finally, regarding pH scale. I do not understand why the authors switches between NBS and total scales. I'll stick with one and note there is big uncertainty in either one when salinity is extreme (that is* pH_T *doesn't work for river water and* pH_{NBS} *doesn't work fully for seawater). Also, pH was given as in "NIST units". This is not the right way we marine chemists will say. It should be in "NIST scale" (I would just call it "in NBS scale"). When saying a pH change then you can say "a change of 0.xx pH units". There is not such a name called NIST or NBS or total units. It is scale!*

We will use only the total scale for pH and convert all freshwater pH to total scale before presenting them in the manuscript. We will not call them units.

33. *Since the ms is an open access discussion paper, I also asked a colleague who knows statistics better than me to read it. Below is her comments. I have read these and generally agreed.*

    Page 6 Line 10: the positive bias, root-mean squared error of the model output is 0.16 for pH and 0.51 for the saturation state of aragonite. The authors claim that these errors are sufficiently small to support the model use for the process studied in the paper. I am not sure about this claim. The error of 0.51 looks big enough to me from my understanding of acidification impacts. The model may be good in reproducing the physical field and biology bloom as the authors stated here.

    A regression with R^2 *of 0.1 without a P value is impossible for readers to judge whether the regression is significant or not (Fig. 3b). If the regression is not significant, TA is not flow dependent, and then the model can't use this relation to derive a scenario. For the regression-based scenarios, since data vary greatly, uncertainties associated with these regressions should be provided and transferred to the model outputs. Without knowing the uncertainties, considering the error of the model output of the saturation state of aragonite, 0.51, not so small, it is hard to evaluate the duration of* $\Omega_A < 1$ *in any scenario. The authors may specify how low* Ω_A *is in these scenarios.*

    Figure 3b and all TA data collected using outdated methods or in freshwater where organic alkalinity uncertainty is high will be removed. We will define new sensitivity scenarios to include more recent and newly acquired data where possible and reduce (and sometimes remove) the dependence on data in which we have less confidence (such as data collected using outdated methods or river TA with high organic alkalinity uncertainty). We will also base our flow-dependent scenarios based on theoretical weathering curves spanning the range of observations rather than statistical fits. We will re-run all the simulations with these new scenarios.

    The model Ω_A uncertainty of 0.51 is large as reviewer 2 mentions, but also positively biased and thus does not overestimate the severity of aragonite undersaturation. We will reword our discussion of the model evaluation to emphasize the bias rather than the uncertainty as our motivation to go forward using the model in this study.