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Interactive comment on "The sensitivity of estuarine aragonite saturation state and pH to the carbonate chemistry of a freshet-dominated river" *by* Benjamin L. Moore-Maley et al.

Anonymous Referee #2

Received and published: 30 November 2017

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. My dissatisfaction is further aggravated by the frustration in reading it at every step. First, 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). Second, the coupled physical and biological ROMS model (first part of the paper) and the simple mixing (second part) are not very compatible. I like that they want to extrapolate the study to a global discussion. However their "transport" of the Fraser conditions to other rivers are clearly

not a good idea. What I like least is the assumption of all rivers have a greater than 1.02 DIC:TA ratio. Many of the problems of this paper came from this assumption but the authors actually generalized their only partially correct conclusions. For example, 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 TAf, ..." First, this statement is only true in the situation the authors created that is the ratio of river DIC:TA = 1.02 to 1.1. In this case, the higher the TAf, the more DIC is in the river water, so river water pH is low. Also it will take more seawater (that is at a higher salinity) to reduce the DIC:TA ratio to a certain value. Thus it is not "high TAf" but a high (DIC-TA) or DIC:TA in river water that is important here and is the reason behind the phenomenon. In the low TAf case, the same DICf:TAf ratio only means a very small DIC in excess of TA in the river water, and it can be very quickly eliminated during river-ocean mixing, or in other word, the pH of the estuarine water is dominated by the seawater. I refer the authors to the paper by Liang et al. 2017 (Marine Chemistry). Further, in extrapolation of the results, the authors didn't consider temperature effect but this effect can also be significant in controlling carbonate system speciation.

Second, the conditions derived from the Fraser River were based on highly uncertainty pHf and TAf data. As the authors correctly recognized that in some rivers organic contribution to the TA can be serious. 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 DICf calculated from the pHf and TAf? Even if Org-Alk is 25%, it would be a serious problem. In the current paper, the extrapolation of the Fraser River DIC:TA ratio globally is just not appropriate. I am not necessarily against making overly simplified assumptions (sometimes one has to), but please fully assess the uncertainty of your assumptions. Here the assumption of DICf:TAf > 1.02 probably not just changes the result slightly it perhaps will change the major conclusion derived. Regarding the data, the authors must clearly say what is new that are not published in their two earlier papers.

Third, the paper is poorly prepared and hard to follow (see my detailed reading notes). Fig. 4 is particularly hard to understand or guess. The authors also often write sentences that are seemingly correct but actually are not so or not clear; this would confuse the readers. For example, p.9, line 10, it says "This asynchrony arises because the response of estuarine carbonate ion over the large range of river TAf and pHf 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 (TAf, pHf and DICf) at the same time. If here "DIC" is not river DIC but internal estuarine, biologically modified DIC, this is probably true, but the authors didn't say that. There are many places, the writing is not transparent to me. So a thorough rewrite with a better readability is also needed.

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 OmegaA 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?

I do not like the implications for future climate. You have speculated too much! (To say high atmospheric CO2 will increase river pCO2 is simply wrong as river pCO2 is generally so much higher than the atm-pCO2.) So simplify it and merge it in the Discussion with just a few sentences.

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

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 (not sure I really need to do this): 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 called global extrapolation.

In addition to the above summary, I also wrote down some notes while reading the text twice (some places many times). Some may be trivial or not fully correct.

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.

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.

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?

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.

p.7, line 11 says "We define our three constant TAf scenarios", then line 17 says "We define our three constant pHf scenarios (Table 2)" (first there is no pHf 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 TAf or pHf", just river endmember scenario 1 to 6 is enough. They have nothing to do with whether TAf is constant with river discharge; they are just your scenarios.

p.7, line 20, I do not understand this– "Given the large seasonal temperature change (>15_C increase in summer), a constant pHf implies a summer DICf decrease due to temperature (causing DICf :TAf to decrease by about 0.06)"âĂŤwhy increased temperature leads to DICf decrease? Is this just a decreased solubility effect or increased river pCO2 leads to more CO2 degassing? Do you mean that under constant pHf and Alkf, higher temperature leads to lower DICf? That is true. But the real question is what is really controlling the pHf at constant TAf but allowing DICf to decrease? You can't just set a certain parameter constant arbitrarily. Anyway you need to explain your as-

sumption. Reading Fig. 5 caption (b), I finally see how you did it. You selected two TAf values one low and one medium-high. Then at each TAf, you selected three pHf values and calculated 6 DICf values. Then you take these 6 TAf and DICf combinations and mix them with the same seawater (TAsw 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 TAf.) My question is– are these combinations realistic? I now take your 6 combinations and put them into CO2SYS (I assume T=15C and all other acid = 0) and verified/confirmed your DICf and DICf:TAf. No problem except that all DICf:TAf ratio > 1.02. This doesn't make sense to me. Perhaps it is true for the low TAf rivers (but in these river the org-ALK is often large), DIC:TA < definitely occurs in medium and high TA rivers.

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.

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)

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.

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

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 TAf and low TAf rivers are likely problematic. Not sure how meaningful is this scenario simulation.

Page 9, Line 8: "Ocean pH and ΩA 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 [Ca2+] 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.

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

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

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

Fig. 6 c &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.

p.11, line 1 and 6 are not consistent. Warming allow more CO2 degassing and decreases river DIC. Yes, I agree. But increased atmospheric CO2 probably won't increase DIC as river DIC is so much higher than the atm-pCO2. If there is any increase it likely increases TA equally (through increase of weathering rate).

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.

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

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 pHT doesn't work for river water and pHNBS 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!

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 R2 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 ïĄŮA <1 in any scenario. The authors may specify how low ïĄŮA is in these scenarios.

References Xue, L., Cai, W. J., Sutton, A. J., & Sabine, C. (2017). Sea surface aragonite saturation state variations and control mechanisms at the Gray's Reef time-series site off Georgia, USA (2006-2007). Marine Chemistry. https://doi.org/10.1016/j.marchem.2017.05.009.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-349, 2017.