

Interactive comment on “The Seasonal Phases of an Arctic Lagoon Reveal Non-linear pH Extremes” by Cale A. Miller et al.

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We would like to thank both anonymous reviewers for their comments and time to help improve this manuscript.

a. We thank the reviewer for this comment and agree there is a utility in scrutinizing the pH-salinity relationship more vigorously. The approach followed by Hagens and Middleburg 2016 derives pH sensitivities as affected by acid-base constituents along with their dependence of speciation on temperature, salinity, and pressure. The relationship of pH to temperature and salinity in this respect would be due to the modulation of dissociation constants and, thus, carbonate chemistry speciation if we assume this to be the dominant acid-base dynamic in the lagoon. Hofmann et al. 2009 examined the sen-

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sitivity of dissociation constants of acid-base speciation to the concomitant effects on proton concentration. They showed that the main driver of pH was the ratio of DIC:AT and a function of conservative mixing. Secondary was biological activity. In this paper, we examined the relationship between pH and temperature as a linear-quadratic. Which is an appropriate approach given the data we have collected.

As mentioned above, quantifying the effects of temperature and salinity on the dissociation constants of the carbonate system and how this modifies pH would be based on using AT data estimated from our AT-salinity regression, thus resulting in a circular approach at determining pH sensitivity to temperature and salinity. For this reason—and as suggested by the reviewer—we find the approach of examining the relationships between running average data more appropriate. Further examination we feel is beyond the scope of this manuscript given the other findings and observations presented.

We have amended the manuscript to reflect our use of this linear relationship approach between pH and salinity and temperature. See lines 349–351, 397–399, 405–406 in the revised manuscript.

We have revised the manuscript to reflect the new findings and make clear that no linear relationships exist with temperature according to our analyses, nor did we find a relationship between salinity and pH during open phase 2018.

Below is the relationship between the 7-d running average for salinity and pH during open phase 2018

We encourage the reviewer to examine figure 3 rather than figure 2 when interpreting the relationships between salinity and pH as figure 3 is a magnified perspective of this data. From this viewpoint, it is more clear that the variability between salinity and pH is non-congruent.

We choose a 7-day running average of the time series because this appeared to give a smoothed line trend that still highlighted small shifts to new baseline pH levels.

C2

New relationships between salinity, temperature, and pH were examined and 7-day running averages were applied to salinity and temperature as well for the times series figures.

b. We find the reviewer's suggestion beneficial and agree that we can discuss the potential mechanisms of CO₂ flux variability to a greater depth. We note though that since we, unfortunately, do not have additional data such as transmissivity (which would be beneficial), most of our conclusions are speculative.

We had not thought to correlate flux with current speed, however, when reexamined we found no correlation between the two and feel it would not add more to the current figure as is.

We found supporting evidence in the literature regarding the reviewer's comment re upwelled CO₂. We have incorporated these points into the discussion. See lines 676–683 in revised manuscript. Briefly, we highlight that previous studies (Åberg et al. 2010) have found that storm events create an upwelling of CO₂ and erosion of stratified layers and conclude that upwelled CO₂ to the surface layers is greater than the CO₂ loss to the atmosphere. These findings support our conclusions and we feel have improved our conclusions regarding the disequilibrium being the driving factor of CO₂ off-gassing.

Given the already lengthy abstract, we feel that additional commentary on CO₂ flux would not entice readers. However, we changed the title to reflect our conclusions regarding CO₂ flux.

c. We have added this additional value of integrated C flux over the entire calendar year which provides a better metric for comparison to other published literature. This value is 1.4×10^{-4} Tg C yr⁻¹. In addition, we have added the suggestion by the reviewer to include the potential implications this finding may have as ice-free days increases in the coming decades. See line 705 in the revised manuscript.

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d. We have added additional detail regarding the frequencies associated with daily irradiance and tides. See lines 299–300 in revised manuscript.

Title: We have changed the title to “The Seasonal Phases of an Arctic Lagoon Reveal the Discontinuities of pH Variability and CO₂ flux at the Air-sea Interface”

L. 56: We have defined LTER

L. 59: We have amended this sentence and those similar that only reported a magnitude change to include the actual pH values.

L. 65: We have added '(from sea to atmosphere)'.

L. 66: We have clarified this to be depth and enclosure differences.

L. 105: We clarified this to be deep pacific water and surface freshwater

L. 108: We have changed this sentence to state 'decrease' rather than 'low'.

L. 110: We clarified that these estimates are specific to aragonite.

L. 118: We do not feel capital P is out of the ordinary (e.g., Hales et al. 2016 and Waldbusser et al. 2015) and have chosen to keep this formatting.

L. 146: We have changed this to 'storm activity'.

L. 186: We have added labels for the two other lagoons.

L. 207: Yes, sediment was collected for these months. The dates are reported in supplementary table 1.

L. 235: We thank the reviewer for providing the additional references here. Lueker overestimates PCO₂ (< 40 uatm) compared to Cai and Wang constants for water masses with low salinity however, these appear to be mostly compensatory approx. -20 uatm with the underestimation of K1 and K2 constants due to low temperatures (~ 5–10 C).

We note that the pH NBS scale used for lower salinity waters underestimates pH val-

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ues relative to Lueker, which incorporates the differences caused by potentiometric measurements and liquid-junction potential at high ionic strength. Given the broad spectrum of salinity values captured during the open phases in this lagoon, there is no one ideal derivation. Quantification of this uncertainty is difficult, however, any potential relative discrepancy would be trivial given the large deviation between duplicate bottle samples.

We have added additional reference to the use of the Lueker constants and acknowledged the potential uncertainties and difficulty in quantifying these. See lines 240–247 in revised manuscript.

L. 279: This refers to properly setting the window, or size of the main lobe (i.e., frequency peak), so the width of the frequency peak does not obscure adjacent frequency peaks.

We have added clarification to this. See line 292 in revised manuscript.

L. 290: Removing points below the freezing line = Removing erroneous data (occurs because something, usually sediments, block the electrical field of the conductivity sensor and conductivity reads erroneously low). We have clarified this in the text.

L. 305: The map has been changed to show these features.

Eq 2: This was following the nomenclature and aesthetics used in Wanninkof 2014 but is not necessary. These have been removed.

End of section 2.5: Please see response to Reviewer # 2 question 2.

Fig 6: We are slightly confused by this comment. The x-axis is salinity and is marked as such on the figure. The color scale is temperature and is also marked appropriately.

In the end: We find that the porewater measurements may be useful for follow-up studies on this system. By presenting them here they become more easily accessible by providing potential benefit to future studies.

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Please also note the supplement to this comment:

<https://bg.copernicus.org/preprints/bg-2020-358/bg-2020-358-AC1-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-358>, 2020.

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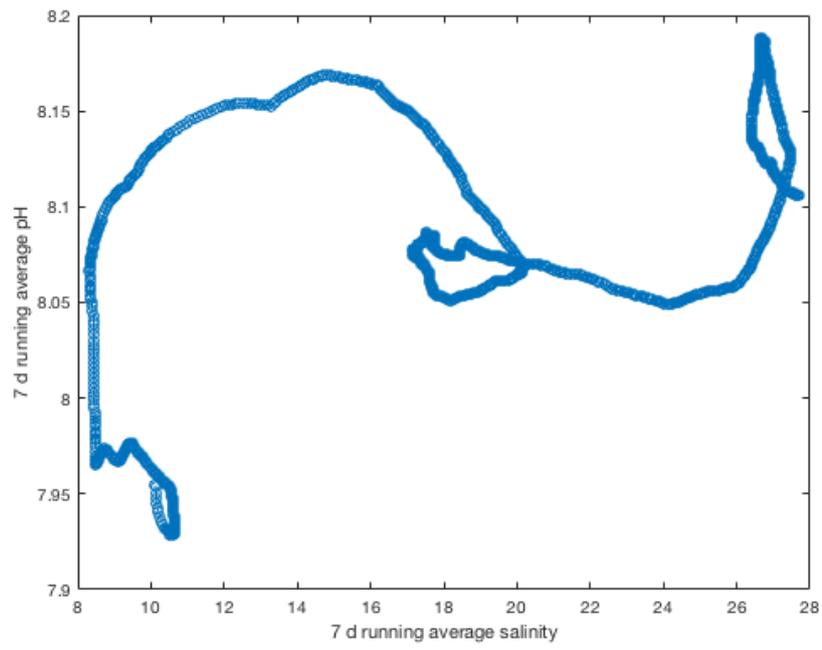


Fig. 1.