

Interactive comment on “The recent state and variability of the carbonate system of the Canadian Arctic in the context of ocean acidification” by Alexis Beaupré-Laperrière et al.

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Author Responses to Leif Anderson (Referee)

Reviewer comments are marked as RC and author responses as AR

RC0: This manuscript includes a very thorough data assessment of the carbon system parameters in Canadian Arctic waters and clearly shows the large variability both in time and space. It confirmed already published conclusions that much of Arctic shallow waters are undersaturated with respect to calcium carbonate, especially aragonite. The basis for this fact is both lowering of salinity by river runoff and sea ice melt in the

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summer, as well as degradation of organic matter, both in the runoff and in the shelf seas. A valuable contribution is evaluation of “time of emergence” that shows the need for several decades of data in order to separate variability from trends.

AR0: We thank the reviewer for his encouragement and incisive comments.

RC1: Another novel approach is to compute the biological contribution to DIC time variations in the top 25 m, i.e. how much of the ocean acidification signal that is of biological activity. They find this to be about one quarter; a number that I argue has to be taken with great care. The reason is that the DIC-reference computation assumes a constant difference in air-sea pCO₂ with time. They mention this but do not relate this assumption to the sea ice coverage before and at the time of measurement. In this region of very temporal variation in sea ice coverage this could have a substantial impact. In the manuscript the decrease in sea ice coverage in the Canadian Basin is mentioned as a cause of elevated uptake of atmospheric CO₂, so the authors are aware of this aspect. One could use the satellite images to assess potential changes in the sea ice cover of the region at the times of interest, if these data have enough spatial and temporal coverage. Considering the fact of changing sea ice coverage I am not sure that the statement on line 504 that the calculated delta DIC-bio is beyond the uncertainty.

AR1: The reviewer points out an important fact that is not specifically mentioned in the manuscript: the uncertainty associated with the change in sea-ice cover is not explicitly stated as being a part of our assumption of constant air-sea pCO₂ gradient. Nonetheless, quantifying it at specific locations over different timespans is a study in of itself and entails great complexity, especially in a dynamic environment such as an archipelago: beyond simply estimating the amount of ice cover at a given location from aerial or satellite footage, one would have to account for ice advection, advection of CO₂ in the underlying water column, and estimate how the change in ice cover modulates air-sea gas exchange, both physically and via local chemical changes during ice formation and decay, such as with brine rejection; (see Rysgaard et al., 2011). We consider the

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quantification of these processes to be fraught with uncertainties and largely beyond the scope of our study. Finally, it is worth noting that, for logistical (navigation) reasons, sampling of the water column most often took place under limited ice cover.

We thus propose to explicitly state that the change in sea-ice cover likely represents a considerable source of uncertainty on Δ DIC_{BIO}, clarify what the uncertainty we mention represents (the uncertainty propagation from the raw data analytical uncertainty and through the calculations), replace or clarify any ambiguous statements such as “beyond the uncertainty”, and caution the reader about the conclusions drawn from this quantity.

Rysgaard, S., Bendtsen, J., Delille, B., Dieckmann, G., Glud, R., Kennedy, H., Mortensen, J., Papadimitriou, S., Thomas, D. & Tison, Jean-Louis. (2011). Sea ice contribution to the air–sea CO₂ exchange in the Arctic and Southern Oceans. *Tellus B*. 63. 10.3402/tellusb.v63i5.16409.

RC2: Further, the computation of Δ DIC_{bio}, as described from line 480, is described in a complicated way. I had to read this section several times before understanding what had been done. My understanding is that DIC_{ref} is computed from TA and pH_t at the starting date, and then corrected for the increase in DIC by the increasing atmospheric pCO₂, assuming a constant air-sea Δ value. This could be described in a straight forward way.

AR2: The reviewer’s understanding is correct and we will simplify the explanation of this parameter in the revised manuscript using a similar phrasing.

Generally this manuscript is well written, but there are several more elements that need more care.

RC3: In line 48 it reads “of these phenomena”. What do these refer to?

AR3: It refers to the different chemical reactions that we collectively label as ocean acidification. This will be clarified in the revised manuscript.

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RC4: Line 109 reads “and expanding undersaturation”. Of what? I assume omega, but as CO₂ is also discussed in this section one has to be explicit.

AR4: Correct, undersaturation of seawater with respect to aragonite. This will be clarified in the revised manuscript.

RC5: Line 165. m-Cresol purple was used for pH determination. Specify if it was purified version or not as this have significant impact on the accuracy, even when calibration against TRIS buffer. Information on the magnitude of correction of the measured value after calibration should be added.

AR5: Over the years, we have used both unpurified and purified (purchased from Prof. Robert Byrne) m-cresol purple. The stated accuracy of our spectrophotometric pH measurements is based on the reproducibility of thousands of pH measurements carried out with both m-cresol purple and phenol red, thus independent measurements, throughout most of the water column over the years. As the pH of surface waters are often higher than deeper in the water column, the absorbance ratio of the phenol red indicator in the former is high (> 3.5) and therefore outside the optimal range of its use. Hence, pH measurements in surface waters are typically based solely on m-cresol purple absorbance ratio measurements. In a recent study across a range of salinities (in a fjord), Delaigue et al. (2020) reported “The salinity-dependence of the dissociation constants and molar absorptivities of the indicators were taken from Robert-Baldo et al. (1985) for phenol red and from Clayton and Byrne (1993) for m-cresol purple. Results computed from these parameters yielded results that were more similar to each other as well as to potentiometric glass electrode measurements than the revised equation for the purified m-cresol purple provided by Douglas and Byrne (2017).”

Clayton, T. D., and Byrne, R. H.: Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results, *Deep-Sea Res. Pt. I*, 40, 2115-2129, 1993.

Delaigue, L., Mucci, A., and Thomas, H.: Spatial variations of the CO₂ fluxes in the

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Saguenay Fjord (Québec, Canada) and results of a water mixing model. *Biogeosciences*, 17, 547-566, 2020

Douglas, N. K., and Byrne, R. H.: Achieving accurate spectrophotometric pH measurements using unpurified meta-cresol purple, *Mar. Chem.*, 190, 66-72, 2017.

Robert-Baldo, G. L., Morris, M. J., and Byrne, R. H.: Spectrophotometric determination of seawater pH using phenol red, *Anal. Chem.*, 57, 2564-2567, 1985.

RC6: In line 228 DIC-bio is mentioned before it has been defined. Hence move it to the section where it is defined.

AR6: As suggested by the reviewer, this sentence will be moved to the appropriate section in the revised manuscript.

RC7: Sentence starting on line 242 does not specify depth range. I assume it refers to the surface water, and if so it should be specified.

AR7: The salinity difference mentioned in this sentence applies to most of the water column. The depth range will be explicitly stated in the revised manuscript.

RC8: Line 258. I don't see the meaning in giving mean values of here as the range is so large and the mean is very much depending on the number of samples included in the different sub-regions. This also refers to the data on line 295.

AR8: Means of aragonite and calcite saturation states are indeed dependent on the number of samples included and the spatial distribution of stations in each sub-region. Nonetheless, means inform the reader on which area has generally lower or higher surface omega values. Simply stating ranges paints an even more incomplete picture of reality, as it would be possible for most values to be close to the minimum or the maximum.

RC9: Sentence starting on line 282 is confusing. What do you rule out? That air-sea exchange has not increased the omega value, or that primary production has not?

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Specify.

AR9: We rule out diurnal fluctuations of biological activity as an explanation for the omega minima we observe (the hypothesis that the lowest values would be observed during the night). This will be clarified in the revised version of the manuscript.

RC10: When it refers to Fig. 7 in the text it would be useful to also give the letters of the individual sub-figures.

AR10: This is a good suggestion; it will be applied to the revised manuscript.

RC11: Line 311. I assume that the pCO₂ and pH-t values are at in situ temperature, but it would be nice to have this specified.

AR11: It will be specified in the revised manuscript.

RC12: The statements starting with the sentence on line 355 needs some more explanations. As salinity is not presented (more than as averages in the table) the reader cannot judge the statement of weaker stratification. So how does this weakening agrees with the statement on line 359 of low salinities from freshwater accumulation followed by efficient mixing? I would assume that addition of freshwater to the surface would strengthen stratification and thus hampering mixing. Please clarify.

AR12: A brief description of the salinity data will be added to this section for the Queen Maud Gulf stations to better illustrate the weaker stratification, or a figure will be added. See Figure 1 of this response for the salinity profiles. Whereas one of the salinity profiles in the area shows that stratification may be stronger because of a very low surface salinity (SP=22) due to riverine input, stratification is generally weaker in this area. The addition of freshwater to the surface and factors that result in more efficient mixing (shallow depth, stronger tidal mixing, hypothesized high residence time of water) all have competing effects on stratification, but are not mutually exclusive. Thus, we do not consider this to be a contradiction, but will address it in the revised manuscript.

RC13: Line 362. It states that the entire water column is undersaturated, but in the

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figure not all are. Same goes for line 549 in conclusions. Change.

AR13: These sentences will be clarified to something akin to “The Queen Maud Gulf is the only area where, at some locations, the water column is entirely unsaturated with respect to aragonite”.

RC14: Sentence starting on line 439. Such conditions would gain on being compared with the dominating atmospheric pressure fields at the time (and before) the observations.

AR14: We appreciate the suggestion but consider it outside the scope of our study that is mostly focused on water chemistry.

RC15: Suggestion ending the paragraph on line 449. I would challenge this explanation as the 2004 pCO₂ data seems quite close to atmospheric levels, while the 2008 data are substantially below. Also the data at 140 m (?) show a difference between the years that is similar. The two options to get undersaturated CO₂ is cooling or primary production. How do you get this signature down to 300-400 m depths? I can only see that there must be two different water masses present (if the data are correct that I do not doubt).

The vertical carbon export we called upon to explain the difference in pCO₂ at depths of 300-400m between 2004 and 2008 referred to the particulate organic carbon that settles from the surface and is metabolized by bacteria at depth. After further consideration, we acknowledge that this explanation might be unlikely, as the greater pCO₂ undersaturation observed near the surface (top 50m) in 2008, relative to 2004, may imply that surface primary productivity was greater in 2008. If gravitational export of biogenic carbon export was responsible for the transfer of metabolisable carbon at depth, pCO₂ should be higher in 2008 at 300-400m, when the opposite is observed. The salinity and temperature data, shown in figure 2 of this response, are nearly identical in 2004 and 2008, which is not consistent with a shift in water masses/stratification or cooling. Alkalinity values at 300-400m depth in 2008 are abnormally high, which

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might explain the low pCO₂ values. Nonetheless, a verification of the specific alkalinity at similar depths in surrounding stations revealed no systematic error. Therefore, we currently cannot propose a plausible explanation for the low pCO₂ values observed at this station in 2008. We will outline this in the revised manuscript.

RC16: Line 464. Make 2 and A subscript in pCO₂ and omega A AR16: This will be modified in the revised manuscript.

RC17: Line 608. The statement that the interannual variability should be relatively small at these depths is not necessarily true. In this dynamic region the contribution of different water masses might vary significantly also at these depths.

AR17: True; a caveat will be added to this sentence. The point made in this sentence nonetheless remains, that is, interannual variability is expected to be smaller at these depths relative to the surface.

RC18: Finally I was surprised that there is no reference to the below article that is highly relevant to this contribution. Azetsu-Scott, K., A. Clarke, K. Falkner, J. Hamilton, E.P. Jones, C. Lee, B. Petrie, S. Prinsenber, M. Starr and P. Yeats, 2010. Calcium carbonate saturation states in the waters of the Canadian Arctic Archipelago and the Labrador Sea. *Journal of Geophysical Research*, 115:C11021, doi:10.1029/2009JC005917.

AR18: This article was part of the literature review and should indeed be cited in the article. It will be cited in section 1, where we describe the state of knowledge on carbonate mineral saturation states in the study area.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-29>, 2020.

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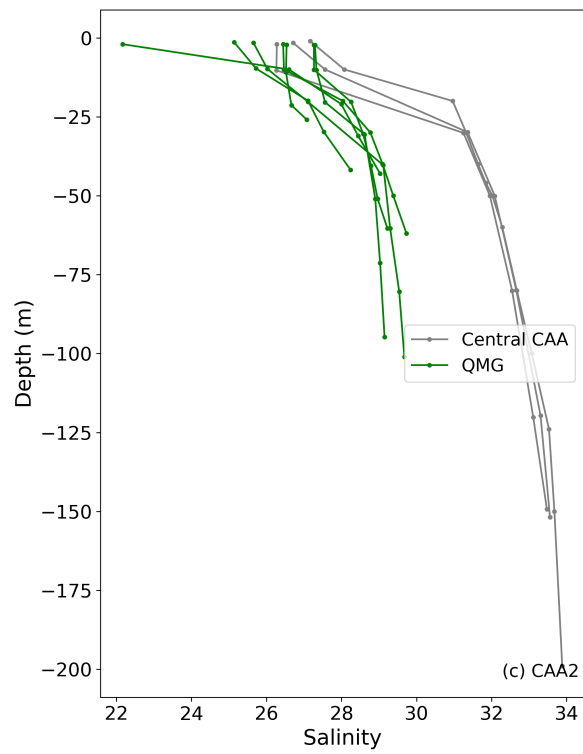


Fig. 1. Salinity profiles in the central CAA (Canadian Arctic Archipelago) and QMG (Queen Maud Gulf)

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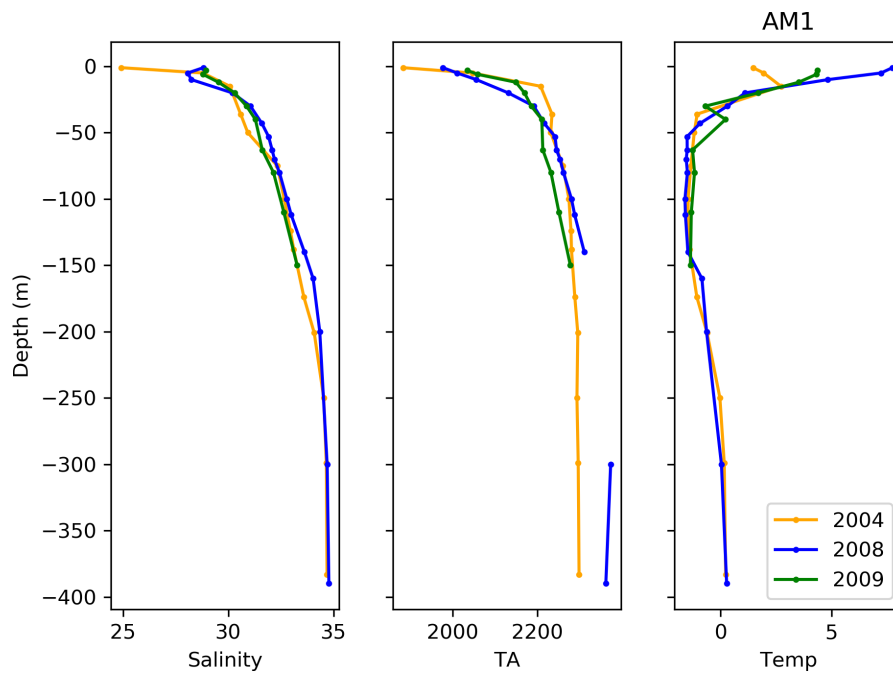


Fig. 2. Salinity, Total alkalinity ($\mu\text{mol/kg}$) and Temperature (degrees C) profiles at station AM1

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