

# ***Interactive comment on “Ocean acidification in the North Atlantic: controlling mechanisms” by Maribel I. García-Ibáñez et al.***

**Anonymous Referee #1**

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## General comments

This manuscript deals with the identification and quantification of the main drivers of pH changes in the Iceland and Irminger basins between 1981 and 2015. To do so, high-quality data of 13 research cruises were combined, quality-checked and statistically analysed. Moreover, the contribution of Cant to changes in DIC was calculated and the change in pH was decomposed into five factors that were numerically estimated.

The manuscript is generally well written, and the results are, in my opinion, scientifically sound. My most pressing comments concern the exact methodology on quantifying the main drivers of pH changes, more specifically the use of Equation 2 and the construction of Table 3. I recommend publication after taking into account the following questions and comments.

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## Specific comments

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- title: The title is somewhat too general in my opinion. The manuscript doesn't focus on the whole North Atlantic, just the Irminger and Iceland basins. Also, the controlling factors for the pH change are determined. I'd therefore suggest changing the title into: "Ocean acidification in the Irminger and Iceland basins (of the North Atlantic): mechanisms controlling pH changes' or equivalent.

- l. 63-64: 'Here...measurements' I would change this sentence in various ways. First, 'an extended period' sounds a bit vague. Better state: 'for a 34-year period'. Second, OA is a term used for collective CO<sub>2</sub> chemistry changes, while you only quantify the drivers of pH change. This must be made clear here. Third, here would be a good place in the manuscript to already shortly mention how these drivers were identified (i.e. by decomposing the observed pH change into five numerically estimated factors)

- Methods: It is not clear to me if there were cruises where more than two variables were concurrently measured and if so, how these were handled throughout the manuscript in terms of internal consistency. Line 75 implies that such overdetermined stations were present and I'd suggest adding to Table 1 which parameters were measured at each cruise. In the way I understand it, for all samples DIC was measured, and one or both of the variables AT and pH was measured. In the case pH or AT was not measured, it was calculated or estimated from the regression algorithm, respectively. Figures 2c,d,f show these data. The remainder of the calculations (Sects. 2.2 and 2.3), however, only use DIC and AT (i.e. the data presented in Figures 2d and f) and calculate pH from these two variables. If I'm correct, please add this to the manuscript more clearly. If I'm incorrect, please provide a clearer description of which variables were used for which analysis.

- l. 99-100: Is a confidence interval of  $2\sigma$  or 95% used throughout the manuscript? If so, please add.

- l. 117-119: This statement needs some more explanation. What is 'preformed AT'

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and how is it determined?

- I. 131, Table 2: why is pH at 25°C used for this uncertainty analysis, while the remainder of the manuscript deals with values at in situ temperature? Assuming a near-steady state as the authors do, it shouldn't matter which of the two is used.

- I. 150-151: Why is this interval of 50-100 dbar chosen? What is the mixed layer depth in these basins? And is this replacement of the upper layer data also done for the construction of Figure 2? This should be made clear.

- I. 155-157: In combination with the caption of Table S1, this statement is somewhat confusing. Only from this caption I understood that pH in Table S1 (and also Figure 3, and  $d\text{pH}/dt_{\text{obs}}$  in Table 3) was calculated from DIC and TA rather than interpolated from measured pH values. This is important information that needs to be part of the main text. Moreover, I'm curious as to whether the authors have tried correcting the measured pH values for the mean pressure of the layer cf. Millero (1995) and how this compared to the average pH estimated using this method.

- I. 161: Does a change in salinity also include the effect due to a change in borate? If so, what salinity – borate relationship is used? This information should also be added to Sect. 2.1.1.

- I. 166, eq (2): Why is  $\delta\text{pH}/\delta\text{DIC}$  not split into  $\delta\text{pH}/\delta\text{C}_{\text{ant}}$  and  $\delta\text{pH}/\delta\text{C}_{\text{nat}}$ ? This is one of the few points of the manuscript that is really unclear to me. The authors should be able to vary  $\text{C}_{\text{ant}}$  while keeping  $\text{C}_{\text{nat}}$  constant and thus calculate these factors separately.

- I. 167-173: It is important that the authors clearly state how they calculated the data presented in Table 3. Therefore this section needs some improvement. I assume that  $d\text{var}/dt$  is calculated based on the regression lines presented in Figures 4-6 (which are based on annually interpolated data). It remains unclear, however, how  $\delta\text{pH}/\delta\text{var}$  is estimated. It is important to realise that  $\delta\text{pH}/\delta\text{var}$  is not a constant parameter, its value calculated from the 1981 data will be substantially different from that calculated

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based on the 2015 data (see, e.g. Riebesell et al., 2009). What is the 'mean pH' the authors refer to in l. 167? (and, similarly, what is the 'real average value of var')? Is it the mean pH of a certain layer of the 34-year period or the mean pH of that layer for each (annually interpolated) year? I assume it is the latter, and therefore it would be very interesting to see the temporal evolution of all the partial differentials over time. Could the authors add these data to the manuscript or supplementary information? Presenting the temporal evolution of these 'buffer factors' can also aid the discussion in Sect 3.2.

- l. 212: An explanation is required of what the 'saturation of Cant' involves. I saw later that it is explained in l. 294-297, so I would move this explanation forward to Sect 3.1. In terms of Eq. 1, would a saturated Cant mean that  $\Delta C_{bio}$  and  $\Delta C_{diseq}$  are 0?

- l. 236-240: I believe that the authors should elaborate on why their pH decrease in the Irminger basin is so different from the values presented by Bates et al. (2014), rather than just stating that the Bates et al. (2014) value 'is exceptionally high compared to the other time series summarized here'. The work of Bates et al. (2014) is also done on seasonally detrended time series and the obtained rate of change is statistically significant ( $P<0.01$ ), so the fact that the results of both analyses are so different should be the basis for an interesting scientific discussion. Bates et al. (2014) link the high rate of pH decrease in the Irminger Sea directly to the high rate of pCO<sub>2</sub> increase at this site; it would be interesting to read the authors' opinion on this.

- l. 240-245: I don't feel that the comparison with the Pacific adds much to the manuscript.

- l. 252-254: Perhaps the authors could additionally evaluate their trends at 25°C for comparison with this study, as it would be very interesting to see the differences resulting from the various data interpolation methods.

- l. 267: Mostly or fully thermodynamic? What other, non-thermodynamic effect could be there?

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- I. 296: Why are data from Mauna Loa used here and not from a more closely located measurement station?
- I. 304: Perhaps clarify that even though salinity also changes (in concurrence with AT), the salinity effect on pH is still negligible.
- I. 311-312: What about changes in the production / respiration balance? Could they also be responsible for the observed Cnat changes?
- I. 333-334: It is not physically meaningful to talk about percentages when discussing contributions to a change in pH, as pH is on a logarithmic scale. Use absolute values or percentages of changes in  $[H^+]$  instead. This also applies to Table 3.
- Figure 2: How is this figure constructed, what is the order of interpolation here? Were the data linearly interpolated over time before the mean was calculated at each sampling point? Or was the mean calculated using the spatio-temporally integrated data? This information needs to be added to the figure caption and/or the Method section.
- Table 3: How are the confidence intervals calculated here? Also, be more explicit about the difference between  $dpH/dt_{obs}$  and  $dpH/dt_{model}$  throughout the manuscript (see also comment on Eq. (2)).

## Technical corrections

- I. 37: shouldn't 1750 be 1850?
- I. 43-44: I feel that the number of references is too high here, since biological effects are not studied in this manuscript
- I. 53-54: also here the number of relevant references could be reduced, though it is less problematic here than in the previous section
- I. 62: remove 'the' in 'the Cnat uptake'

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- l. 67: should be '2.1.1' (same applies to '2.1.2' on l. 74 and '2.1.3' on l. 105)
- l. 76: remove 'the' in 'the total alkalinity'
- l. 113: replace 'less' by 'minus' (also in l. 116)
- l. 166, Eq (2): add the subscript 'model' to the left hand side, to be consistent with the right column of Table 3 (distinguishing more clearly between  $d\text{pH}/dt_{\text{obs}}$  and  $d\text{pH}/dt_{\text{model}}$  could be done throughout the manuscript)
- l. 169: replace ' $\delta\text{var}/\delta t$ ' with ' $d\text{var}/dt$ ', these are ordinary differentials.
- l. 288: move 'dominates' to the end of the sentence.
- l. 304: 'in last instance' is not very clear. Do you mean 'in a net sense'?
- l. 325: remove 'however', this sentence is not contradictory with the previous one
- Table 1: for each cruise, add which carbonate system parameters are measured
- Table 3: why are the last digits in the column describing the salinity effect on pH presented with subscripts?
- General comment on the figures: be consistent with the amount of significant digits on the colour bar and/or y-axis (e.g. 35.3 vs. 35.25 for Figure 1b). This applies to all figures in the manuscript
- Figure 1a: the colour scheme is not very clear, the light-dark gradient could be more extreme
- Figures 3-6: some general comments on these figures: please use different symbols for the different water masses, this makes the figures readable on black & white. Also, add the title of the basin on top of the figure (Irminger basin left column, Iceland basin right column), this makes the figures more accessible without having to read the caption. Finally, the dotted lines (annually interpolated values) are hardly visible.
- Figures 4 and 6: '(b and c)' should be replaced with '(b and d)'

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## References

Riebesell U., Körtzinger A. and Oschlies A. (2009) Sensitivities of marine carbon fluxes to ocean change. *Proc. Natl. Acad. Sci. U. S. A.* 106, 20602–20609.

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