Reply to Referee #1

We thank referee #1 for the helpful comments. We have addressed the referee's concerns as explained below.

- 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.

Following your suggestion and suggestions from Referee #2 we changed the title into "Ocean acidification in the Subpolar North Atlantic: rates and mechanisms controlling pH changes".

- 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 CO2 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)

Following your suggestions we changed this sentence into "Here we quantify the pH change for a 25-year period and identify its chemical and physical drivers by decomposing the observed pH change into five numerically estimated factors (temperature, salinity, alkalinity, anthropogenic CO_2 and non-anthropogenic CO_2), all based on direct measurements". Note that the timeframe of the study has decreased to 25 years since, following suggestion of Referee #2, TTO data was excluded from our study.

- 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.

Sorry for the confusion. We added the suggested column to Table 1. We also added some explanatory comments in the 2.1.2 section (Ocean CO_2 chemistry measurements). The first sentence was changed to: "The twelve cruises selected for our study have high-quality measurements of the seawater CO_2 system variables (Table 1)", since there are cruises with DIC measurements only. We also added the following sentence to clarify how we obtain DIC values when not available: "For the cruises where direct DIC measurements had not been performed, it was computed from A_T and pH using the thermodynamic equations of the seawater CO_2 system (Dickson et al., 2007) and the CO_2 dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987)."

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

> *Thank you for your comment. We noticed that we were using incorrectly the term 'confidence interval'. In lines 99-100 the term 'confidence interval' was not correctly used and, therefore, it was deleted. In the revised manuscript we have replaced the term 'confidence interval' with 'standard deviation'. We only used the confidence intervals in figures 3-6, where we defined what we use as confidence interval (2x(standard deviation)/$\sqrt{N}$, where N is the number of samples), which is a 95% confidence interval since the samples are independent.*

- l. 117-119: This statement needs some more explanation. What is 'preformed AT' and how is it determined?

> *We added the following explanation at the end of the paragraph: "The A_T^0 is based on the concept of potential alkalinity ($PA_T = A_T + NO_3 + PO_4$) and is defined as $A_T^0 = PA_T - (NO_3^0 + PO_4^0)$ (Vázquez-Rodríguez et al., 2012a), where NO_3^0 and PO_4^0 are the preformed nitrate and phosphate concentrations, respectively. NO_3^0 and PO_4^0 are determined as $NO_3^0 = NO_3 - AOU/R_{ON}$ and $PO_4^0 = PO_4 - AOU/R_{OP}$. In the former equations AOU stands for Apparent Oxygen Utilisation, which is the difference between the saturated concentrations of oxygen calculated using the equations of Benson and Krause (1984) and the measured concentrations of oxygen; R_{ON} and R_{OP} are the Redfield ratios proposed by Broecker (1974)".*

- l. 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.

> *The purpose of Table 2 is to give an estimate of the reproducibility of the analysis and calculation methods. This reproducibility gives insights about the goodness of the data for trend analysis. Since trends are determined using pH at in situ conditions, we followed your suggestion and we changed the pH reported in Table 2 to pH at in situ conditions.*

- l. 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.

> *Following the comment of Referee #2 about the same issue, we have slightly changed the methodology and now we removed the data from the photic layer (pressure < 75 dbar). We also removed this upper data to construct figures 1 and 2.*

- l. 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 dpH/dt_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.

> *We are sorry for the confusion. In fact, pH in Table 3 and Figure 3, and in the newly added Table S2 of the Supplementary Information, was calculated as you state. Therefore we changed the statement of lines 155-157 by the following*

statement, hoping that it is clearer now: "The exception comes with pH_{Tis}*, which is pressure sensitive, and for which we needed to define a unique reference pressure to remove pressure effects due to varying sampling strategies.* pH_{Tis} *was calculated using the layer average values of DIC and* A_T *for the considered year but using the time-averaged pressure of the layer over the studied time period as reference pressure".*

Regarding the pressure correction proposed by Millero (1995), we did not perform this correction to our data. Millero's corrections were developed to correct the data before computer power was sufficient enough to perform the proper calculations. In our study, we took the advantage of the CO2SYS software (Lewis and Wallace, 1998; van Heuven et al., 2011), making not necessary the use of the corrections proposed by Millero (1995).

Lewis, E. and Wallace, D. W. R.: Program developed for CO_2 *system calculations, 30 ORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, TN, 1998.*
van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., and Wallace, D. W. R.: MATLAB program developed for CO_2 *system calculations, ORNL/CDIAC-105b, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, TN, 15 doi:10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1, 2011.*

- l. 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.

Yes, the change in salinity includes the effect due to borate change since when changing salinity A_T *and DIC are maintained constant. Regarding the salinity-borate relationship, we used the constants recommended by Glodap v2 and by the 'Guide to Best Practices for Ocean* CO_2 *Measurements' of Dickson et al. (2007), which are the constants of Uppström (1974). We added the following clarifying statements in reference to this doubt: "Changes in temperature and salinity influence the equilibrium constants of the oceanic* CO_2 *system. Additionally, changes in salinity influence the borate concentration, whose influence is taken into account by the relationship proposed by Uppström (1974)".*

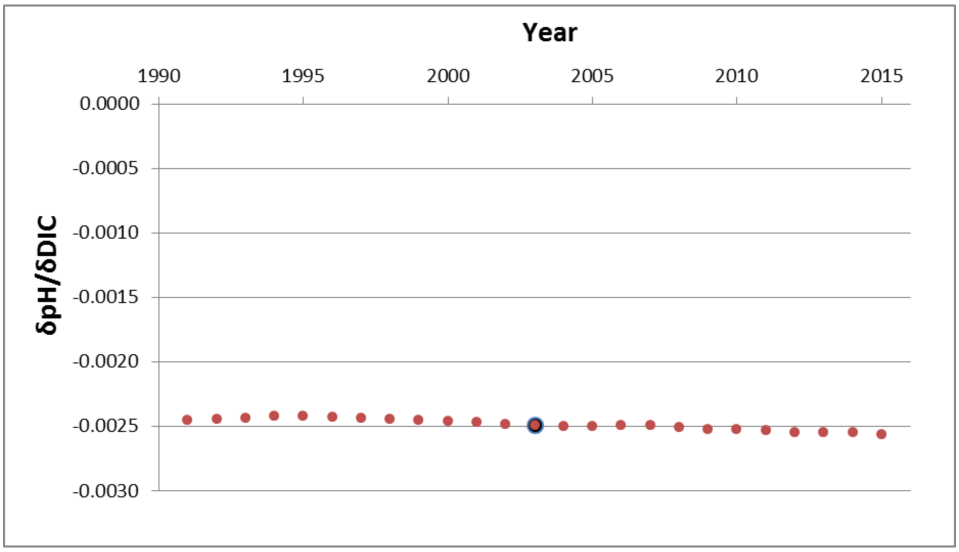
Uppström, L.R.: Boron/chlorinity ratio of deep-sea water from the Pacific Ocean, Deep-Sea Res., 21, 161–162, doi:10.1016/0011-7471(74)90074-6, 1974.

- l. 166, eq (2): Why is δpH/δDIC not split into δpH/δCant and δpH/δCnat? This is one of the few points of the manuscript that is really unclear to me. The authors should be able to vary Cant while keeping Cnat constant and thus calculate these factors separately.

We did not split δpH/δDIC because the change in pH per unit of DIC is going to be the same if the DIC molecule is C_{ant} *or is* C_{nat}*. Hence, we think it is not necessary to split the 'buffer factor' between* C_{ant} *and* C_{nat}*. We added the following clarifying statement: "Note that sensitivity of* pH_{Tis} *to changes in* C_{ant} *is the same as the sensitivity to changes in* C_{nat} *since both are DIC, and, therefore, only* $\frac{\partial pH_{Tis}}{\partial DIC}$ *is necessary".*

- l. 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 dvar/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 δpH/δvar is estimated. It is important to realise that δpH/δvar is not a constant parameter, its value calculated from the 1981 data will be substantially different from that calculated 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.

> *As stated on lines 171-173, trends of all variables involved in Eq. 2 (and therefore in Table 3) were calculated using the annually interpolated data. As you stated, dvar/dt were calculated based on regression lines presented in Figures 4-6. Regarding the terms ‘δpH/δvar’, we calculated the pH for each layer and year (also for the interpolated years, without cruises) keeping all but the parameter in question constant and equal to the mean value for the layer over the study time period. With an example, if we want to calculate δpH/δS, what we do is to calculate a pH for each layer and year using the average S value for each layer and year but the mean values for each layer over the studied time period (1991-2015) for the rest of variables (T, A_T and DIC). To make this clearer in the text, we changed the sentence in lines 167-173 by: “To estimate $\frac{\partial pH_{Tis}}{\partial var}$ (where var refers to each of the drivers: T_{is}, S, A_T and DIC) we calculated a pH_{Tis} for each layer and year using the layer average value of var for each year but keeping the values of the other drivers constant and equal to the time-average value for the layer over the studied time period”.*
>
> *We are aware that the ‘buffer factors’ change with time and that the system is not linear. However, since we split the studied region in different layers, the range of variation of the parameters within each layer during the studied time period is small (the ± of Table S1 gives insights about this small variability), and then, we can assume linearity. Also because of the small range of variation of the parameters within each layer, the range of variation of the ‘buffer factors’ is also small, and we can neglect their change when calculating the change in pH due to each of the proposed controlling mechanisms. I am enclosing an example about the change of ‘δpH/δDIC’ in the SPMW layer of the Irminger basin. The red points show the ‘δpH/δDIC’ values for each year, and the black point is the ‘δpH/δDIC’ used in the study. As you can see, the change of ‘δpH/δDIC’ over time is negligible, and the value used in the study is the mean value for the period 1991-2015.*



> *We added the following statement to clarify this question in the manuscript: "Given that the variability of the physicochemical properties within each layer is relatively low (see standard deviations of the averaged values in Table S1), we can assume that these derivatives are constant over the studied time period and use a constant derivative value for each layer".*

- 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 ΔCbio and ΔCdiseq are 0?

> *We added a similar explanation to that found in lines 294-297 ("approximately 80% of the C_{ant} concentration expected from a surface ocean in equilibrium with the atmospheric CO_2"). Regarding the doubts about Eq. 1, the term ΔC_{diseq} is never 0 since it depends on the conditions of the water mass at the time of its formation. It is known that water masses are not in complete equilibrium with the atmospheric CO_2 concentration when formed (see Matsumoto and Gruber, 2005). Besides, a disequilibrium in the C_{ant} content with respect to the atmospheric C_{ant} is expected, since ocean in uptaken C_{ant}. Therefore, the surface layer is never saturated in C_{ant}. To sum up, a water mass can be saturated in oxygen, and hence ΔC_{bio} is 0, but ΔC_{diseq} is never 0.*
>
> *Matsumoto, K. and Gruber, N.: How accurate is the estimation of anthropogenic carbon in the ocean? An evaluation of the ΔC* method, Global Biogeochem. Cycles, 19, doi:10.1029/2004GB002397, 2005.*

- 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 pCO2 increase at this site; it would be interesting to read the authors' opinion on this.

> *We added the explanation given by Bates et al. (2014): "Bates et al. (2014) linked the high acidification rate found at the Irminger Sea time-series to the high rate of increase in DIC (1.62 ± 0.35 $\mu mol\cdot kg^{-1}\cdot yr^{-1}$) observed at this site, which is almost twice our rate of increase in DIC (0.64 ± 0.07 $\mu mol\cdot kg^{-1}\cdot yr^{-1}$, Fig. 5c). This is based on data from only one site, further north than our section, and indicates that spatial variations are substantial in this region". We do not have enough information to elucidate other possible explanations.*

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

> *Following suggestions of Referee #2, we are going to keep this comparison, adding some extra information.*

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

> *The fact that precludes comparing trends is not the difference in the temperature to which pH is referenced, but the fact that Vazquez-Rodriguez et al. (2012b)*

normalized pH values to climatological potential temperature, salinity, silicate and AOU (WOA values). This normalization eliminates part of the influence of these parameters (potential temperature, salinity, silicate and AOU) on the pH trends. This is why direct comparison between their pH trends and our pH trends is difficult. However, we added some text comparing the trends reported by both works: "This normalization, combined with the different temporal coverage (1981–2008), causes the rates reported by Vazquez-Rodriguez et al. (2012b) differ from those obtained in the present work. The pH_N *trends reported for the SPMW and uLSW layers of the Irminger basin and for the ISOW layer of the Iceland basin are very similar to our* pH_{Tis} *trends for these layers. However, the* pH_N *trends reported by Vazquez-Rodriguez et al. (2012b) for the cLSW layer in both basins and for the ISOW layer in the Irminger basin are significantly different from our* pH_{Tis} *trends for these layers, but are very similar to pH changes derived from* C_{ant} *changes (*$\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}$ *in Table 3). In the case of the DSOW layer, the* pH_N *trend is also in agreement with* $\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}$ *trends. This suggests that the normalization carried out by Vazquez-Rodriguez et al. (2012b) could remove some of the impact of the natural component (represented here by* C_{nat}*) over pH changes, essentially due to the use of AOU in the normalization".*

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

We eliminated mostly, because referee is right, all the effect is thermodynamic.

- l. 296: Why are data from Mauna Loa used here and not from a more closely located measurement station?

Stations closer to the location of our study area, e.g., Mace Head, do not have the same time-coverage as our study. Therefore, we changed the pCO_2 *data to the 'Globally averaged marine surface annual mean data' from the NOAA (ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_annmean_gl.txt), since* pCO_2 *in the atmosphere is almost homogeneous worldwide, and hence the degree of saturation does not change.*

- l. 304: Perhaps clarify that even though salinity also changes (in concurrence with AT), the salinity effect on pH is still negligible.

We added the following clause to line 304: "(as stated before, the effect of salinity change on pH is negligible)".

- l. 311-312: What about changes in the production / respiration balance? Could they also be responsible for the observed Cnat changes?

Now that we are not taking into account the photic layer (see answer to comment about 'l. 150-151'), changes in C_{nat} *cannot be brought about by changes in production. Besides, what we refer to as 'changes related to the ventilation of water masses' involves both changes in the renewal of the water mass with upper waters and changes in the respiration. To make this clear, we added the following statement when describing the general pattern of* C_{nat} *distribution (section 3.1): "The* C_{nat} *distribution has an opposite pattern, with low surface values and high bottom values (Fig. 2g), similar to that of the AOU distribution (Fig. 2e), since* C_{nat} *is linked to the ventilation of water masses, i.e., respiration and renewal of the water mass".*

- l. 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.

> *We are aware that pH is on a logarithmic scale, but for the small range of pH change to which we are working, we can consider that pH follows a linear scale. That is why the use of percentages is meaningful. Besides, we found that the percentage of change in terms of $[H^+]$ is exactly the same than that calculated in terms of pH (for the reasons explained above). Finally, the scientific community is working in terms of pH. For all these reasons we decided to keep this work in terms of pH. We added the following statement to the 2.3 section: "Due to the small range of pH change to which we are working and to the relatively low pH variability within each layer, we can consider that pH follows a linear scale instead of a logarithmic scale. This causes that the contributions of each of the terms considered in Eq. (2) to pH change are equivalent to the contributions in terms of $[H^+]$".*

- 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.

> *Figure 2 was built by loading all the cruise data to a single section plot on the ODV, and then a DIVA gridding was performed. Since the purpose of describing Figure 2 is giving a general view of the properties along this section, we think that describing a single cruise is enough. For this reason, we decided to describe the general distribution of the main variables along the section using the 2004 cruise as reference. This cruise represents the mean year of the studied period. In this way we avoid interpolating the data from all cruises to a single grid and then averaging them to build Figure 2, with all the errors that this would entail.*

- 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)).

> *The ± were calculated by propagation of errors of the slopes of each of the derivatives. We also added some explanatory comments throughout the manuscript to distinguish more clearly between dpH/dt_obs and dpH/dt_model, changing the later by dpH/dt_total.*

Technical corrections

- l. 37: shouldn't 1750 be 1850?

> *We do not think so. We have chosen 1750 according to Caldeira and Wickett (2005).*
>
> *Caldeira, K. and Wickett, M.E.: Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean, J. Geophys. Res., 110, C09S04, doi:10.1029/2004JC002671, 2005.*

- l. 43-44: I feel that the number of references is too high here, since biological effects are not studied in this manuscript

> *We eliminated three references.*

- l. 53-54: also here the number of relevant references could be reduced, though it is less problematic here than in the previous section

We eliminated two references.

- l. 62: remove 'the' in 'the Cant uptake'

Done.

- l. 67: should be '2.1.1' (same applies to '2.1.2' on l. 74 and '2.1.3' on l. 105)

Thank you for catching this typo. We made the corresponding corrections.

- l. 76: remove 'the' in 'the total alkalinity'

Done.

- l. 113: replace 'less' by 'minus' (also in l. 116)

Done.

- 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 dpH/dt_obs and dpH/dt_model could be done throughout the manuscript)

We changed dpH/dt_model by dpH/dt_total, and introduced this new term to Eq. (2) and Table 3. We also added some explanatory comments throughout the manuscript to distinguish more clearly between dpH/dt_obs and dpH/dt_total.

- l. 169: replace 'δvar/δt' with 'dvar/dt', these are ordinary differentials.

Thank you for catching this typo. We made the correction.

- l. 288: move 'dominates' to the end of the sentence.

Done.

- l. 304: 'in last instance' is not very clear. Do you mean 'in a net sense'?

Yes, we meant 'in a net sense'. We changed the expression.

- l. 325: remove 'however', this sentence is not contradictory with the previous one

We changed 'however' by 'thus' as suggested by Referee #2.

- Table 1: for each cruise, add which carbonate system parameters are measured

Added

- Table 3: why are the last digits in the column describing the salinity effect on pH presented with subscripts?

They were presented because they are not significant. However, we decided to present them without subscript.

- 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.

For figures built with ODV (i.e., Figures 1 and 2) is not possible to change the amount of significant digits in the color bars. For the remaining figures, the amount of significant digits has been updated.

- Figure 1a: the colour scheme is not very clear, the light-dark gradient could be more extreme

> *Figure updated following your suggestions.*

- 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 were updated following your suggestions. We decided to remove the dotted lines.*

- Figures 4 and 6: ‘(b and c)’ should be replaced with ‘(b and d)’

> *Thank you for catching this typo. We made the corresponding corrections.*