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)." - 1. 99-100: Is a confidence interval of $2*\sigma$ 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.

- 1. 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 CO₂ 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 CO₂ 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 salinityborate relationship, we used the constants recommended by Glodap v2 and by the 'Guide to Best Practices for Ocean CO₂ 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 CO₂ 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 $\delta pH/\delta DIC$ not split into $\delta pH/\delta Cant$ and $\delta pH/\delta Cnat$? 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 $\delta pH/\delta DIC$ 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".

- 1. 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 $\delta pH/\delta var$ is estimated. It is important to realise that $\delta pH/\delta var$ 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 1. 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 ' $\delta pH/\delta var$ ', 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 $\delta pH/\delta S$, 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 \pm 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 ' $\delta pH/\delta DIC$ ' in the SPMW layer of the Irminger basin. The red points show the ' $\delta pH/\delta DIC$ ' values for each year, and the black point is the ' $\delta pH/\delta DIC$ ' used in the study. As you can see, the change of ' $\delta pH/\delta DIC$ ' 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 Δ Cbio and Δ Cdiseq 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.

- 1. 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 ($1.62 \pm 0.35 \mu mol \cdot kg^{-1} \cdot yr^{-1}$) observed at this site, which is almost twice our rate of increase in DIC ($0.64 \pm 0.07 \mu mol \cdot kg^{-1} \cdot yr^{-1}$, 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.

- 1. 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.

- 1. 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.

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 $\left(\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}\right)$ 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".

- 1. 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 (<u>ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2 annmean gl.txt</u>), 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". - 1. 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 \pm 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

- 1. 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.

- 1. 62: remove 'the' in 'the Cant uptake'

Done.

- 1. 67: should be '2.1.1' (same applies to '2.1.2' on 1. 74 and '2.1.3' on 1. 105)

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

- 1. 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.

- 1. 288: move 'dominates' to the end of the sentence.

Done.

- 1. 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.

- 1. 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.

Reply to Referee #2

We thank referee #2 for the helpful comments. We have addressed the referee's concerns as explained below.

General comments:

- Consider adding "Subpolar" to North Atlantic in the title.

Added.

- I believe your results are occasionally strongly affected by the TTO data (particularly in the Irminger basin), conceivably worsened by your time-interpolation performed to 'provide weight to old cruises'. I recommend publication of your results with exclusion of TTO data, or least mention in the text of how such exclusion would affects results.

Thank you for your suggestion. We recalculated all the trends excluding TTO data and the difference between pH trends with and without TTO were significant. Hence, we decided to exclude the TTO data from our study, with all the changes that it entails.

- The sections plots of Fig1 and Fig2 are unrealistically noisy. The captions suggests the "mean distributions" are plotted, but these are not averages, but rather all data of all cruises thrown into a single section, with inappropriately short influence radii for the contouring (or whatever the equivalent terminology is for DIVA gridding). They thus represent not natural spatial heterogeneity, but temporal aliasing. This leads to disturbingly jittery artifacts (particularly evident in Fig2d as blue/purple/pink patchwork). Consider either contouring true averages, or simply increasing the influence radii (i.e., smooth it more).

Thank you for your suggestions. You are right, what we did is plotting the data of all cruises in a single section, rather than averaging the data. 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.

- Consider adding a visually catchy and informative summarizing section plot (one for pHobs, or perhaps one per pH-driver), showing per water mass the rate of pH change. In each, surface layers would most red, as would DSOW, with intermediate layers slightly lower, and Iceland on average lower than Irminger.

Thank you for your suggestion. We added the suggested pHobs figure to the supplementary information (Figure S1).

Specific comments:

- Consider capturing some more cruise details in your Table 1. For instance, please tabulate the type of measurements performed on each cruise (which had pH directly, which calculated it – i.e., you lines ~75–100). What is the consequence of the rather seriously sounding, but nonchalantly made remark in line 91 "However, Carter et al reported a pH inaccuracy of 0.0055"? Is that a positive or negative bias? Systematic for everyone or just for them? Do you compensate?

We added an extra column that specifies the measurements performed on each cruise. What we wanted to highlight with the sentence in line 91 is the fact that although it is possible to achieve high reproducibility in pH measurements, all the measurements will have an inherent uncertainty of 0.0055 due to the uncertainty in the determination of the constants of the tris-buffer. Therefore, the 0.0055 quantity is an uncertainty that affects all pH measurements, which we cannot compensate. We have clarified this point by changing the highlighted sentence to: "However, Carter et al. (2013) reported an inherent uncertainty of spectrophotometric pH determinations of 0.0055 pH units, associated to the trisbuffer used for calibration". (See also answer to comment about line 131).

- line 113: less => minus

Corrected

– line 120: "advantages" relative to what? ΔC^* ?

Yes. We added the following statement at the end of the sentence: "relative to the previous method proposed by Gruber et al. (1996)".

- line 121: I can't follow. The suggestion is that no Cant-free reference waters are required, but it's not clear why that is. Consider explaining more clearly or not at all and only keeping the reference to VR2012).

We changed the statement to make it clearer: "And second, the parameterizations of A_T^0 and ΔC_{diseq} are determined using the subsurface layer as reference (Vázquez-Rodríguez et al., 2012a), where the age of the water parcel and, therefore, its C_{ant} concentration is estimated using CFC measurements (Waugh et al., 2006)".

- line 131: explain why you consider 0.0055 the "accuracy" of the pH measurements. Again, if Carter thinks this is a /systematic/ error of the method, that would not affect detectability of trends.

You are right; this uncertainty will affect all pH measurements and, therefore, will not affect the detectability of trends. What we wanted to highlight with this statement is that the data we are using have high reproducibility (higher than the accuracy of the measurements) and thus are suitable for determining trends. We added the following statement to the manuscript: "The high reproducibility, an order of magnitude better than the uncertainty (0.0055 pH units, Carter et al. (2013)), is suggestive of high quality data". (See also answer to comment about line 91).

- I find the use of statistical terminology confusing. The terms "standard deviation", "confidence interval" and seem to be used loosely or even interchangeably while they each have a clearly defined use case. (Line 99-100 seems to suggest that you equate "two standard deviations" to "confidence interval"). If the use of these terms is nonetheless is correct then certainly the employed confidence level should be mentioned to make sense of the stated confidence intervals. I particularly object to referring to the standard deviation of depths in a defined depth (or density) range as the 'confidence interval' of depths (first column of T1).

Thank you for your comment; we noticed that we were using the term 'confidence interval' incorrectly. In lines 99-100 the term 'confidence interval' was not correctly used and, therefore, it was deleted. In the revised manuscript we changed the term 'confidence interval' with 'standard deviation'. We, therefore, change the numbers presented in the tables accordingly. We also eliminated the standard deviation of the pressure data in Table 2 as you suggested. We only used the confidence intervals in figures 3-6, where we defined what we consider as confidence interval $(2x(standard deviation)/\sqrt{N}, where N is the number of samples), which corresponds to a 95% confidence interval since our samples are independent.$

– I hold the whole of line 125-140 to constitute a slight misuse of statistical numbers. The reasoning here seems to be "the spread between the means of cruises is smaller than the spread within each cruise, and thus we believe we can detect trends between cruises". Although the closeness in cruise means is certainly comforting, that alone does not make for detectability of trends. It would at best provide a lower bound for the detectability of trends (i.e., trends within the ranges given in T1 would go unnoticed but might nonetheless exist). Consider adding a small statement that indicates these results are suggestive of high quality, and try to avoid suggesting to provide evidence thereof.

Thank you for your suggestions. We agree with your comment. We changed lines 139-140 as follows: "The high reproducibility, an order of magnitude better than the uncertainty (0.0055 pH units, Carter et al. (2013)), is suggestive of high quality data. Using these standard deviations for the seven cruises, and taking into account the 25 years considered in this study, the threshold of detectability of pH trends at 95% of confidence is 0.00012 pH units·yr⁻¹, which renders confidence to the estimated trends".

- line 150: this 'replacement' process is a little rash. I can imagine ignoring these shallow data, but simply overwriting them with data that has less sensitivity to seasonality without providing a compelling case for doing so is not warranted. I do not believe that ignoring the 100m surface layer would yield a vastly different result to what you now got. If that is indeed so, I recommend using that ignore-approach, to avoid the suggesting that you're fudging.

Thank you for your suggestion. We followed it by removing the photic layer (pressure < 75 dbar) from our study, so as to avoid the seasonality effect. This depth was determined by the depth of the seasonal nutrients drawdown. Thus, we replaced sentence in line 150 by the following sentence: "To reduce the influence of seasonal differences in sampling on the inter-annual trends, only samples with pressure \geq 75 dbar were considered. The 75 dbar level was determined by the depth of the seasonal nutrients drawdown along the section".

- line 154: please be specific in how you "take into account thickness and separation". I presume that the average of tall profiles with large spacing to east and west get higher weight in average-of-averages? Do you have a specific reason for not using the alternative approach of averaging per layer the 'grid boxes' of Fig2? Presumably you did not grid the data for analysis but only for figure making.

You are right when highlighting the different weighting given to the profiles in function of their spacing, but, intuitively, horizontally gridding with a linear interpolation would give the same result as the method used in our study.

We did not grid the data horizontally but vertically, and this vertical gridding was taken into account for both figure building and calculations. Averages were then performed in an area-weighted basis, so that accounting for the irregular spacing between stations. This was performed by using a trapezoidal integration, which produces the same results as the horizontally gridding, which consumes more computational time.

– I'm not clear on what you've done here. I agree that pressure-adjustment here is necessary, although heaving of even 500 m would not even produce a pH shift larger than 0.02 units. However, you'd do this also simply to reduce the range of pH values within each (non-horizontal) water mass. I would, however, believe the proper procedure to be (i) "recalc pH for each sample in water mass to pH at the single mean depth of that watermass (for the cruise or the whole dataset, that shouldn't matter much) and then (ii) calculate average of these recalculated pH values. This might be what you did, but the way I read it, you first calculated the average pH, and then shifted that average pH to the 'correct' depth. If so, consider redoing more appropriately, or explain for daft readers like myself why the used approach *is* appropriate.

Sorry for the misunderstanding of our methodology. What we did was calculate an average pH for each layer and year from the average values of DIC and A_T , and referred to the mean pressure of the layer over the studied time period. We rewrote this explanation in the manuscript: "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". We have also corroborated that the methodology you propose and the methodology that we applied give the same results. This is because the variability of the physicochemical properties within each layer is relatively low, and therefore the system is linear. Following this line of reasoning we added the following sentence in the first paragraph of section 2.2: "The advantage of working in layers is the relatively low variability of the physical and chemical properties within the layers, allowing us to assume linearity in the ocean CO_2 system". We, then, decided to keep our methodology since it is simpler and working with averaged DIC and A_T (conservative) is desirable instead of working with recalculated pH (not conservative) values for each sample and then averaging them. Besides, the recalculated pH for each sample that you propose will not reproduce the pH shown in Figure 2c.

- line 157: remove last four words "over the pH trends"

Done.

– I can't fully comprehend what the approach is that was followed in section 2.3. The idea is clear "keep all but one parameter constant and see how pH changes. The sensitivity of pH to an increase in DIC would be sharper in 2015 than in 1981. Is that accounted for in the method? Specify the calculation routine you used.

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 \pm 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 ' δ pH/ δ DIC' in the SPMW layer of the Irminger basin. The red points show the ' $\delta pH/\delta DIC$ ' values for each year, and the black point is the ' $\delta pH/\delta DIC$ ' used in the study. As you can see, the change of ' $\delta pH/\delta DIC$ ' 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".

- Consider restructuring 2.3 into a distinct paragraph for the determination of time trends and one for inferring strength of individual drivers. Your TABLE3 mentions the "sum of drivers" or "model", which terminology is nowhere used in the text, please harmonize. Also, T3 separates influence of Cnat and Cant, but Eq2 does not.

We included a table in the Supplementary Information that shows the strength of individual drivers (Table S2). Since time trends are represented in figures 4-6, rebuilding section 2.3 would involve citing figures 4-6 before figure 2, which we think this is not a logical order for figures in the manuscript. However, we added the following statement to the results section to clarify where the reader can find the derivative values: "The values of each term of $\frac{\partial pH_{Tis}}{\partial var}$ and $\frac{dvar}{dt}$ (where var refers to each of the drivers) described in Sect. 2.2 can be found in the Supplementary Table S2 and in Figs. 4-6, respectively".

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_model and dpH/dt_total.

We slightly changed Eq. (2) to clearly indicate the separation between C_{ant} and C_{nat} : $\left(\frac{dpH_{Tis}}{dt}\right)_{total} = \frac{\partial pH_{Tis}}{\partial T_{is}}\frac{dT_{is}}{dt} + \frac{\partial pH_{Tis}}{\partial S}\frac{dS}{dt} + \frac{\partial pH_{Tis}}{\partial A_{T}}\frac{dA_{T}}{dt} + \frac{\partial pH_{Tis}}{\partial DIC}\left(\frac{dC_{ant}}{dt} + \frac{dC_{nat}}{dt}\right)$

- line 168: "real average value" => "observed linear trend" (???)

What we meant is the average value calculated for each layer and cruise. We changed the sentence to the following to make this clearer: "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".

- TABLE1: I believe "confidence interval" here is "standard deviation", or is it truly CI? Then state the confidence level. I'm not sure the CI of the average of averages, or however one would call the last row, has any statistical meaning – why not simply provide SD in that row? You use pH25 in table 1, while stating in the text that pHisT and pH25 are not easily compared – why the sudden use of pH25 here?

We believe you are referring to Table 2. We changed 'confidence interval' by 'standard deviation' and we changed the results accordingly. The purpose of this table is to give an estimate of the reproducibility of the analysis and calculation methods, which we take as an indicative of the goodness of the data for trend analysis. Regarding the scale of pH, since trends are performed using pH at in situ conditions, we followed your suggestion and we changed the pH reported in Table 2 by pH at in situ conditions.

- FIGURE1: some of the contour intervals have at sig1 or sig2 label, while caption and text suggest cutoffs were based on sig0.

Sorry for the confusion, sig θ would refer to all the sigma levels, either referenced to 0, 1000 or 2000 dbar. To make this clearer we changed the figure caption by "(referenced to 0 dbar, σ_0 ; 1000 dbar, σ_1 ; and 2000 dbar, σ_2 ; all in kg·m⁻³)"

- I generally very much like your other (time-tested) figures. Perhaps increase coverage of fig 1a to provide a view of distance to land on eastern extent of section.

We updated Figure 1a following your suggestions. We increased the eastward extension of the map.

– Consider moving 3.1 to the introduction.

We appreciate your suggestion. However, and despite the qualitative nature of this section, we think it fits better in the results section rather than in the introduction, since it is a description based on our data. Besides, it provides useful information for understanding the sections coming next. In view of this, we decided to keep this section as it is.

– line 209: "almost homogenous" – sections plots suggest otherwise, see earlier comment on influence radii

After changing Figure 2 as suggested in the previous comment regarding this figure, now the statement is true.

- line 211: "because they are correlated" – that relationship is not causal, please rephrase.

You are right. We eliminated this statement, so that, in our opinion, the explanation of property distributions is improved.

– line 212: can you qualify that "80%" in light of the mentioned Δ Cdiseq? Is this what one would expect?

The existence of a saturation lower than 100% in the surface layer is expectable for an oceanic uptaken of C_{ant} (see Matsumoto and Gruber, 2006). Therefore, a disequilibrium in the C_{ant} content with respect to the atmospheric C_{ant} is expected.

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.

– line 239: can you speculate on the possible causes for the supposedly spuriously high rate of pH decrease observed by Bates et al at IrmSTS?

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 ($1.62 \pm 0.35 \ \mu mol \cdot kg^{-1} \cdot yr^{-1}$) observed at this site, which is almost twice our rate of increase in DIC ($0.64 \pm 0.07 \ \mu mol \cdot kg^{-1} \cdot yr^{-1}$, 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.

- line 244: you mention a tropical Pacific time series station, and contrast it with your work and a subpolar Pacific TSS, latter two match nicely. Add a brief sentence attributing that contrast.

Now that we are not including the TTO cruise data in our study, our trends are in agreement with the trends found in the tropical Pacific and are slightly higher than the trends found in the subpolar Pacific. We changed the manuscript accordingly to these changes, and we added the following explanation to the low trends found in the subpolar Pacific: "Wakita et al. (2013) attributed the lower than expected pH trends to an increasing A_T trend".

- line 246-254: your statement "renders direct comparison difficult" does not stand up to scrutiny. Recalculating pH to different temperatures does not changes the slope of a pH trend. That is, slopes can be compared (i.e., VR12's Fig3ab vs your Fig3ab), even if absolute values cannot. I recommend more work is made of this comparison, particularly if results between studies differ.

The fact that precludes comparing trends is not the difference in the temperature at which pH is referenced, but the fact that Vazquez-Rodriguez et al. (2012b) normalized pH values to potential temperature, salinity, silicate and AOU in WOA05. 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 $\left(\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}\right)$ 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".

- line 322: if anything, these are 4 decades (80s 90s 00s and 10s). Consider "34-year period" or similar

We changed it by "25-year period", since now we are not considering the TTO cruise.

- line 323 (and likely elsewhere): "separate and increase into its drivers" is slightly sloppy English. Consider rephrasing

We changed the sentence into: "From the study of the main drivers of the observed pH changes...".

- line 325: "However" => "thus". Reduced rate of decrease of pH is what one expects with increasing alk.

Changed.

- line 327: "salty" => "saline"

Changed.

- line 333: consider "observe" => "infer". There's too many interpretative steps involved to call this "observe"

Changed.

Author's changes in manuscript: List of major changes in the revised manuscript

List of major changes in the revised manuscript

- 1) The text has been revised according to all the referees' comments. In particular, the methodology section has been significantly revised to make clearer the procedure followed in our work to achieve the results presented.
- 2) Title has been slightly modified to fulfill the referees' suggestions.
- 3) Data from the older cruise has been excluded from our study.
- 4) Surface data (first 75 dbar) has not been included.
- 5) Comparison with previous works has been extended.
- 6) Map on Fig. 1 has been color updated and eastward extended.
- 7) Figure 2 has been updated and now shows data from one cruise instead of plotting the data of all cruises in a single section plot.
- 8) Figures 3-6 have been updated to make them more readable on black and white version, and titles of the basins have been added on top of the figures.

1 2

Ocean acidification in the <u>Subpolar</u> North Atlantic: <u>rates and</u> <u>mechanisms</u> controlling <u>mechanismspH changes</u>

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15 Abstract. Repeated hydrographic sections provide critically needed data on, and understanding of, changes in 16 basin-wide ocean CO₂ chemistry over multi-decadal timescales. Here, high-quality measurements collected at 17 thirteentwelve cruises carried out along the same track between 19891 and 2015, have been used to determine 18 long-term changes in ocean CO₂ chemistry and ocean acidification in the Irminger and Iceland basins of the 19 North Atlantic Ocean. Trends were determined for each of the main water masses present and are discussed in 20 the context of the basin-wide circulation. The pH has decreased in all water masses of the Irminger and Iceland 21 basins over the past $\frac{3425}{2}$ years, with the greatest changes in surface and intermediate waters (between -0.00 $\frac{0810}{2}$ 22 \pm 0.0001 pH units·yr⁻¹ and -0.001318 \pm 0.0001 pH units·yr⁻¹). In order to disentangle the drivers of the pH 23 changes, we decomposed the trends into their principal drivers: changes in temperature, salinity, total alkalinity 24 (A_T) and total dissolved inorganic carbon (both its natural and anthropogenic components). The increase of in anthropogenic CO₂ (C_{ant}) was identified as the main agent of the pH decline, partially offset by A_T increases. The 25 26 acidification of intermediate waters caused by C_{ant} uptake has been reinforced by the aging of the water masses 27 over the period of our analysis. The pH decrease of the deep overflow waters of the Irminger basin was similar 28 to that observed in the upper ocean, and was mainly linked to the Cant increase, thus reflecting the recent contact 29 of these deep waters with the atmosphere.

30 Keywords. Ocean acidification; C_{ant}; water masses; Subpolar Gyre.

31 **1 INTRODUCTION**

The oceanic uptake of a fraction of the anthropogenic CO_2 (i.e., C_{ant} ; CO_2 released from humankind's industrial and agricultural activities) has resulted in long-term changes in ocean CO_2 chemistry, commonly referred to as ocean acidification, OA (e.g., Caldeira and Wickett, 2003, 2005; Raven et al., 2005; Doney et al., 2009; Feely et al., 2009). The changes in the ocean CO_2 chemistry result in declining pH and reduced saturation states for $CaCO_3$ minerals (e.g., Bates et al., 2014). The average pH ($-log_{10}[H^+]$) of ocean surface waters has decreased by about 0.1 pH units since the beginning of the industrial revolution (1750), and based on model projections we expect an additional drop of 0.1–0.4 by the end of this century, even under conservative CO_2

- 39 emission scenarios (Caldeira and Wickett, 2005; Orr, 2011; Ciais et al., 2013). The rate of change in pH is at
- 40 least a hundred times faster than at any time since the last Ice Age (Feely et al., 2004; Raven et al., 2005), clearly

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- 41 outpacing natural processes in ocean chemistry that have occurred in the past due to geological processes (Raven
- 42 et al., 2005). These changes in ocean CO_2 chemistry will most likely have adverse effects on organisms,
- 43 particularly calcifying ones, on ecosystems (e.g., Langdon et al., 2000; Riebesell et al., 2000; Pörtner et al.,
- 44 2004; Orr et al., 2005; Doney et al., 2009; Gattuso et al., 2014) and on major marine biogeochemical cycles (e.g.,
- 45 Gehlen et al., 2011; Matear and Lenton, 2014).
- The global ocean has absorbed ~30% of the Cant emitted to the atmosphere between 1750 and the present 46 47 (Sabine et al., 2004; Khatiwala et al., 2013; DeVries, 2014; Le Quéré et al., 2015). This Cant is not evenly 48 distributed throughout the oceans (Sabine et al., 2004), but enters the interior ocean preferentially in regions of 49 deep convective overturning and subduction (Maier-Reimer and Hasselmann, 1987; Sarmiento et al., 1992; 50 Lazier et al., 2002). This explains why the Meridional Overturning Circulation (MOC) makes the North Atlantic Ocean one of the most important C_{ant} sinks of the global ocean, storing 25% of the global oceanic C_{ant} (Sabine et 51 52 al., 2004; Khatiwala et al., 2013) despite being only 11% of the global ocean volume (Eakins and Sharman, 53 2010). The MOC transports Cant-laden surface waters from the Equator to the northern North Atlantic Ocean 54 (e.g., Wallace, 2001; Anderson and Olsen, 2002; Álvarez et al., 2003; Olsen et al., 2006; Quay et al., 2007; 55 Zunino et al., 2015b), where deep water formation provides a pathway for Cant into the interior ocean (Lazier et 56 al., 2002; Pérez et al., 2008, 2013; Steinfeldt et al., 2009; Pérez et al., 2013). AsBeing regions close to deep 57 water formation areas and where water mass transformation occurs (Sarafanov et al., 2012; García-Ibáñez et al., 58 2015), the Irminger and Iceland basins are geographically well placed to monitor temporal changes in the 59 Atlantic MOC (Mercier et al., 2015), and to determine the rates of Cant penetration to the deep ocean and its 60 consequence for OA. 61 In this paper, we examine high-quality direct measurements of ocean CO_2 chemistry taken-from thirteentwelve 62 cruises conducted across the Irminger and Iceland basins between 19891 and 2015. Previous studies focused on
- the C_{ant} uptake and its storage and effect on pH in the Irminger and Iceland basins (e.g., Pérez et al., 2008;
 Olafsson et al., 2009; Bates et al., 2012; Vázquez-Rodríguez et al., 2012b). Here we quantify OAthe pH change
 for an extendeda 25-year period and identify its chemical and physical drivers, by decomposing the observed pH
- 66 change into five numerically estimated factors (temperature, salinity, alkalinity, anthropogenic CO₂ and non-
- 67 <u>anthropogenic CO₂), all</u> based on direct measurements.

68 2 MATERIALS and METHODS

69 2.1 Datasets

70 2.21.1 Cruise Information

We used <u>data from thirteentwelve</u> cruises along the same track across the Irminger and Iceland basins, with the cruise dates spanning <u>3425</u> years (19<u>89</u>1–2015; Table 1, Fig. 1a). The bottle data were accessed from the merged data product of the Global Data Analysis Project version 2 (GLODAPv2; Olsen et al., 2016) at <u>http://cdiac.ornl.gov/oceans/GLODAPv2</u>, except for more recent unpublished data collected during the OVIDE 2012 and 2014 cruises and the 2015 cruise (58GS20150410). The data of the 1991 cruises (64TR91_1 and 06MT18_1) were merged and treated as a single cruise. 77

2.21.2 Ocean CO₂ chemistry measurements

78 At least two variables The twelve cruises selected for our study have high-quality measurements of the 79 seawater CO₂ system were measured on all cruises included in our analyses, but the measured pairs varied between cruises variables (Table 1). The T total alkalinity (A_T) was analysed by potentiometric titration and 80 81 determined by developing either a full titration curve (Millero et al., 1993; Dickson and Goyet, 1994; Ono et al., 82 1998) or from single point titration (Pérez and Fraga, 1987; Mintrop et al., 2000), and were calibrated with Certified Reference Materials (CRMs), with an overall accuracy of 4 μ mol·kg⁻¹. For samples without direct A_T 83 84 measurements, it was estimated using a 3D moving window multilinear regression algorithm (3DwMLR), using 85 potential temperature (θ), salinity, nitrate, phosphate, silicate and oxygen as predictor parameters (Velo et al., 86 2013). The total dissolved inorganic carbon (DIC) samples were analysed with coulometric titration techniques 87 (Johnson et al., 1993), and were calibrated with Certified Reference Materials (CRMs), achieving an overall 88 accuracy of 2 µmol·kg⁻¹. The exception to the use of this analytical technique was the 1981 TTO NAS (Transient 89 Tracer in the Ocean North Atlantic Survey) cruise, where DIC was determined potentiometrically (Bradshaw et 90 al., 1981) and no CRMs were used. The TTO NAS DIC measurements were deemed unreliable (Brewer et al., 91 1986), therefore, the DIC values compiled in the GLODAPv2 merged data product are those calculated from 92 pCO₂-and revised A₁ reported by Tanhua and Wallace (2005). For the cruises where direct DIC measurements 93 had not been performed, it was computed from A_T and pH using the thermodynamic equations of the seawater 94 CO_2 system (Dickson et al., 2007) and the CO_2 dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987). These calculated DIC values have an associated uncertainty of 4 µmol·kg⁻¹, 95 96 calculated by random propagation of the reported A_T and pH accuracies. pH was determined either 97 potentiometrically (Dickson, 1993a, b) using pH electrodes or, more commonly, at 25°C and 1 atm with a 98 spectrophotometric method (Clayton and Byrne, 1993) using either scanning or diode array spectrophotometers 99 and m-cresol purple as an indicator. The spectrophotometric pH determination has a typical precision of 0.0002-100 0.0004 pH units (Clayton and Byrne, 1993; Liu et al., 2011). However, Carter et al. (2013) reported an 101 inaccuracyinherent uncertainty of the spectrophotometric pH determinations of 0.0055 pH units, associated to 102 the tris-buffer used for calibration. When direct pH measurements were not performed, it was computed from A_T 103 and DIC using the thermodynamic equations of the seawater CO₂ system (Dickson et al., 2007) and the CO₂ 104 dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987). For these calculated pH 105 values, we estimated an uncertainty of 0.006 pH units by random propagation of the reported A_T and DIC 106 accuracies. The exception to the latter is the 1981 TTO NAS cruise, whose DIC problems caused the estimated 107 uncertainty for calculated pH values to be slightly higher (0.008 pH units). Ar data from the 1981 TTO NAS cruise were checked against A_T values generated by the 3DwMLR (Velo et al., 2013). A_T values differing by 108 more than two times the standard deviation (confidence interval; 7 µmol·kg⁻¹) of the difference between 109 110 measured A_T and 3DwMLR predicted A_T were replaced with the predicted A_T value. However, for leg 6 of the 111 1981 TTO-NAS cruise (which was not analysed by Tanhua and Wallace (2005)) the limit of substitution for the 112 predicted A_T value was lowered to 4 μ mol·kg⁻¹. Note that the effect of A_T corrections on pH trends is negligible, since A_T corrections of 4 µmol·kg⁻¹ lead to pH changes lower than a thousandth. The pH values reported here are 113 at in situ conditions (of temperature and pressure) and on the total scale (pH_{Tis}). 114

115

2.21.3 Anthropogenic CO₂ (i.e., C_{ant}) estimation

116 C_{ant} concentrations were estimated using the back-calculation method φC_T^{0} (Pérez et al., 2008; Vázquez-117 Rodríguez, 2009a) that has previously been applied for the entire Atlantic Ocean (Vázquez-Rodríguez et al., 118 2009b). Back-calculation methods determine C_{ant} for any sample in the water column as the difference between 119 DIC concentration at the time of the measurement and the DIC concentration it would have had in preindustrial 120 times. Following Gruber et al. (1996), Fthis is represented as the difference in preformed DIC between the time 121 of observation and the preindustrial as:

122 $C_{ant} = DIC_{meas} - \Delta C_{bio} - DIC_{preind} - \Delta C_{diseq},$ (1)

123 where the preformed DIC for the time of observation is represented as the measured DIC (DIC_{meas}) lessminus 124 any DIC added to the water due to organic matter remineralisation and calcium carbonate dissolution ($\Delta C_{\rm bio}$), 125 and the preindustrial preformed concentration is represented by the DIC concentration the water would have if in 126 equilibrium with the preindustrial atmosphere (DIC_{preind}) lessminus any offset from such an equilibrium value, 127 known as the disequilibrium term (ΔC_{diseq}). The procedure requires DIC and A_T as input parameters, and the empirical parameterization of the preformed $A_T (A_T^{0})$ for the computation of the calcium carbonate dissolution 128 and of the ΔC_{diseq} term (Vázquez-Rodríguez et al., 2012a). The A_T^0 is based on the concept of potential alkalinity 129 $(PA_T = A_T + NO_3 + PO_4)$ and is defined as $A_T^0 = PA_T - (NO_3^0 + PO_4^0)$ (Vázquez-Rodríguez et al., 2012a), where 130 NO_3^0 and PO_4^0 are the preformed nitrate and phosphate concentrations, respectively. NO_3^0 and PO_4^0 are 131 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 132 Apparent Oxygen Utilisation, which is the difference between the saturated concentrations of oxygen calculated 133 134 using the equations of Benson and Krause (1984) and the measured concentrations of oxygen; R_{ON} and R_{OP} are 135 the Redfield ratios proposed by Broecker (1974).

136 The $\varphi C_T^{\ 0}$ method presents two main advantages relative to the previous method proposed by Gruber et al. 137 (1996). First, the spatiotemporal variability of $A_T^{\ 0}$ is taken into account. And second, C_{ant} -estimation needs no 138 "zero C_{ant} " reference, since the parameterizations of $A_T^{\ 0}$ and ΔC_{diseq} are determined using the subsurface layer as 139 reference for water mass formation conditions (Vázquez-Rodríguez et al., 2012a), where the age of the water 140 parcel and, therefore, its C_{ant} concentration is estimated using CFC measurements (Waugh et al., 2006). The 141 overall uncertainty of the $\varphi C_T^{\ 0}$ method has been estimated at 5.2 µmol·kg⁻¹ (Pérez et al., 2008; Vázquez-142 Rodríguez, 2009a).

143 The uncertainties and reproducibilities and uncertainties of the main variables analysis and calculation methods 144 were determined from the deep waters sampled at Iberian Abyssal Plain during the seven repeats of the OVIDE 145 line, since these waters are expected to be in near-steady state. The confidence intervalsstandard deviations of 146 those samples for each cruise (Table 2) were taken as an estimate of the uncertainty of the methodologies at each 147 cruise. The uncertainties of the Apparent Oxygen Utilization (AOU; the difference between the saturated 148 concentrations of oxygen calculated using the equations of Benson and Krause (1984) and the measured 149 concentrations of oxygen), A_T and pH on the total scale at 25℃ (pH_{T25})pH_{Tis} for the seven cruises were similar. 150 The confidence intervalsstandard deviations of Cant (1.2-1.62.4-3.2 µmol·kg⁻¹) and pH_{T25}pH_{Tis} (0.0042-0.0063) 151 pH units) across for each of the seven cruises are lower than the inherent uncertainty of the φC_T^{0} estimates (5.2) µmol·kg⁻¹) and the accuracy of the spectrophotometric pH measurements (0.0055 pH units), which provides 152 153 confidence that these data are suitable for trend determination. The confidence intervalsstandard deviations of 154 the Cant estimates are rather similar than into those from other regions where Cant has been compared across many

cruises (i.e., 2.4 µmol·kg⁻¹ in the South Atlantic Ocean, Ríos et al. (2003); 2.7 µmol·kg⁻¹ in the Equatorial 155 Atlantic Ocean, 24°N, Guallart et al. (2015); and 2.7 µmol·kg⁻¹ reported from a transect along the western 156 boundary of the Atlantic Ocean from 50°S to 36°N, Ríos et al. (2015)). The confidence intervalstandard 157 158 deviations of the mean values of the Iberian Abyssal Plain samples across the seven cruises all (last row of Table 159 2) waswere taken as an estimate of the reproducibility of the methodologies. The high 160 reproducibilities reproducibility, an order of magnitude lower better than the uncertainties, render uncertainty 161 (0.0055 pH units, Carter et al. (2013)), is suggestive of high quality data. Using these standard deviations for the seven cruises, and taking into account the 25 years considered in this study, the threshold of detectability of pH 162 trends at 95% of confidence is 0.00012 pH units yr⁻¹, which renders confidence to the estimated trends. 163

164 **2.2 Water mass characterization**

165 Changes in ocean CO₂ chemistry were determined for the main water masses in the Irminger and Iceland 166 basins. These are: (1) Subpolar Mode Water (SPMW); (2) upper and classical Labrador Sea Water (uLSW and 167 cLSW, respectively); (3) Iceland–Scotland Overflow Water (ISOW) and; (4) Denmark Strait Overflow Water 168 (DSOW; Fig. 1b). The layers defining the water masses were delimited using potential density following Azetsu-169 Scott et al. (2003), Kieke et al. (2007), Pérez et al. (2008) and Yashayaev et al. (2008). <u>The advantage of</u> 170 working in layers is the relatively low variability of the physical and chemical properties within the layers, 171 allowing us to assume linearity in the ocean CO₂ system.

172 To better determine the interfaces limits between layers and the average value of each variable in each layer, 173 cruise bottle data were linearly interpolated onto each dbar before determining average variable values, an 174 improvement with respect to the previous approaches of Pérez et al. (2008, 2010) and Vázquez-Rodríguez et al. 175 (2012b). Upper layer data (pressure ≤ 100 dbar) were replaced with the mean value in the pressure range 50–100 176 dbar to reduce the influence of seasonal differences in sampling on the inter annual trends (Vázquez Rodríguez 177 et al., 2012a). Then, the interpolated profiles were divided into the different water mass density intervals (Fig. 178 1b). Next, the variables were averaged over each density layer on a station by station basis for each cruise, 179 defined in Figure 1b. Finally, the average values in each density layer were determined for each cruise taking 180 into account the thickness of the layer and the separation between stations. Note that average values of The 181 exception comes with pH_{Tis}, which is pressure sensitive parameters, i.e. pH_{Tis}, were referred, and for which we 182 needed to the meandefine a unique reference pressure to remove pressure effects due to varying sampling 183 strategies. pH_{Tis} was calculated using the layer average values of DIC and A_T for the considered year but using 184 the time-averaged pressure of the layer over the studied time period to avoid the effects of the heaving of as 185 reference pressure. To reduce the water masses due to warming and/or ofinfluence of seasonal differences in 186 sampling on the sampling strategy over the pHinter-annual trends, only samples with pressure ≥ 75 dbar were 187 considered. The 75 dbar level was determined by the depth of the seasonal nutrients drawdown along the section. 188 The average values of the variables for each layer and their confidence intervalsstandard deviations can be found 189 in the Supplementary Table S1.

190 **2.3 pH deconvolution**

191 Changes in ocean pH may be brought about by changes in in situ temperature (T_{is}), salinity (S), A_T , and/or 192 DIC, of which changes in the latter may be brought about by C_{ant} uptake or by natural processes (C_{nat}), such as

193	remineralisation. Cnat is determined as the difference between measured DIC and estimated Cant. Changes in
194	temperature and salinity influence the equilibrium constants of the oceanic CO ₂ system. Additionally, changes in
195	salinity influence the borate concentration, whose influence is taken into account by the relationship proposed by
196	<u>Uppström (1974).</u>

197To estimate how much each of these altogether five factors have
assumed linearity and decomposed the observed pH changes into these potential drivers according to:

100	<u>арн_{тіз} _ д</u>	pH _{Tis} dT _{is} _	∂pH_{Tis} dS ⊥	∂pH_{Tis} dA_T ⊥	$\frac{\partial p H_{Tis}}{d(C_{nat}+C_{ant})}$		(2)
177	dt -	∂T _{is} dt '	∂s dt '	∂A _∓ dt ′	dDIC dt '		(2)
200	$\left(\frac{dpH_{Tis}}{dt}\right)_{tot}$	$\frac{\partial p H_{Tis}}{\partial T_{is}}$	$\frac{dT_{is}}{dt} + \frac{\partial pH_{T}}{\partial S}$	$\frac{dS}{dt} + \frac{\partial p H_{Tis}}{\partial A_T}$	$\frac{\mathrm{dA}_{\mathrm{T}}}{\mathrm{dt}} + \frac{\partial \mathrm{pH}_{\mathrm{Tis}}}{\partial \mathrm{DIC}} \left(\frac{\mathrm{dC}_{\mathrm{ant}}}{\mathrm{dt}} + \right.$	$\frac{\mathrm{d}C_{\mathrm{nat}}}{\mathrm{d}t}$),	(2)

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⁺].

To estimate $\frac{\partial p H_{Tis}}{\partial war}$ (where *var* refers to each of the drivers: T_{is}, S, A_T and DIC) we calculated the meana pH_{Tis} 205 206 for each layer and eruiseyear using the reallayer average value of var for each year but keeping the values of the 207 other three-drivers constant and equal to the meantime-average value for the layer over all the cruises the studied 208 time period. Given that the variability of the physicochemical properties within each layer is relatively low (see 209 standard deviations of the averaged values in Table S1), we can assume that these derivatives are constant over 210 the studied time period and use a constant derivative value for each layer. 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 211 <u>necessary</u>. To estimate each $\frac{\partial var}{\partial t} dvar}{dt}$ term we performed a linear regression between var and time for each 212 213 layer.

Trends of all variables involved in Eq. (2) were calculated <u>usingbased on</u> the annual interpolation of the observed values to avoid the bias due to the reduced availability of cruises during the 80's and-90's with respect to the 2000's.

217 3 RESULTS AND DISCUSSION

218 **3.1 Mean dD**istribution of water mass properties

219 The Irminger and Iceland basins in the North Atlantic are characterized by warm and saline surface waters, 220 and cold and less saline intermediate and deep waters (Fig. 2a,b). The central waters (here represented by the 221 SPMW layer), which dominates the upper \sim 700 m, are warmer and saltier in the Iceland basin than in the 222 Irminger basin, reflecting the water mass transformation that takes place along the path of the North Atlantic 223 Current (NAC) (Brambilla and Talley, 2008). In particular, the mixing of the SPMW layer with the surrounding 224 waters while flowing around the Reykjanes Ridge (evident in the salinity distribution; see also García-Ibáñez et 225 al. (2015)), in conjunction with the air-sea heat loss, results in a colder and fresher SPMW layer in the Irminger 226 basin. The uLSW and cLSW layers, below the SPMW layer, are-warmer and saltier in the Iceland basin due to 227 their mixing with the surrounding waters during their journey from their formation regions (Bersch et al., 1999; 228 Pickart et al., 2003; García-Ibáñez et al., 2015). The ISOW layer dominates at depths beneath the cLSW layer. This layer is warmer and saltier in the Iceland basin, reflecting its circulation. ISOW comes from the Iceland– Scotland sill and flows southwards into the Iceland basin, where it mixes with the older North Atlantic Deep Water (NADW). Then, it crosses the Reykjanes Ridge through the Charlie–Gibbs Fracture Zone (Fig. 1a), where it mixes with the recently ventilated–cLSW and DSOW, becoming colder and fresher. In the bottom of the Irminger basin, a fifth layer is distinguished, DSOW, being the coldest and freshest layer of the section.

234 The general pattern of pH_{Tis} (Fig. 2c) follows by and large the distribution expected from the surface 235 production of organic material and remineralisation at depth. The<u>Consequently</u>, high surfacepH values (> 8.05) 236 are the result of the withdrawing of DIC by photosynthetic activity, found in upper layers, while the values 237 generally decrease with depth down to < 7.95 in the deepest layers, because of the DIC concentration increase 238 resulting from remineralisation. This overall pattern is disrupted at ~500 m in the Iceland basin by a layer with 239 relatively low pH_{Tis} values (< 7.98), coinciding with relatively high AOU and DIC values (Fig. 2e,f). This layer 240 could be associated to an area of slower circulation where the products of the remineralization of the organic 241 matter accumulate. This thermocline layer could also been influenced by waters of southern origin (Sarafanov et 242 al., 2008), which are advected into the region by the NAC, whose arrivalextension is closely related withto the 243 North Atlantic Oscillation (Desbruyères et al., 2013). The presence of this low pH layer lowers the average pH 244 of our SPMW layer in the Iceland basin compared to the Irminger basin (Fig. 3). An opposite pattern is found in 245 the uLSW layer. The water mass formation occurring in the Irminger basin (Pickart et al., 2003; García-Ibáñez et 246 al., 2015; Fröb et al., 2016; Piron et al., 2016) transfers recently ventilated low DIC and high pH waters to depth, 247 which causes the mean pH of uLSW in the Irminger basin to be higher than in the Iceland basin. Finally, the 248 layers that contain the overflow waters have the lowest pH values. The presence of the older NADW in the 249 ISOW layer in the Iceland basin decreases the mean pH of this layer here, making it lower than in the Irminger 250 basin.

251 The surfaceupper layer waters of the section have low DIC values, which rapidly increase when increasing 252 depth (Fig. 2f). The low DIC values in the uppermost ~200 m are also related to a consequence of the 253 photosynthetic activity that withdraws DIC from seawater. Below ~200 m the DIC distribution is almost 254 homogeneous, only disrupted by relatively high values in the Iceland basin at ~500 m associated with the 255 thermocline layer, and at the bottom, associated with the old NADW. The gradients in DIC anthropogenic and 256 natural components of DIC are much stronger. This is because the Cant and Cant distributions are anti correlated. 257 The C_{ant} values are high, close to saturation (approximately 80% of saturation the C_{ant} concentration expected 258 from a surface ocean in equilibrium with the atmospheric CO_2), near the surface and decrease with depth (Fig. 2h), because C_{ant} enters the ocean from the atmosphere. The C_{nat} distribution has an opposite pattern, similar to 259 260 that of the AOU distribution (Fig. 2e), with low surface values and high bottom values (Fig. 2g), for reasons 261 discussed above similar to that of the AOU distribution (Fig. 2e), since C_{nat} is linked to the ventilation of water 262 masses, i.e., respiration and renewal of the water mass.

The A_T distribution along the section resembles the salinity distribution, with high values associated with the relatively saline central waters and <u>relatively</u> low and almost homogeneous values in the rest of the section (Fig. 2d). The exception comes with the <u>deep watersISOW layer</u>. The high A_T values found in the ISOW layer of the Iceland basin, which have among the highest A_T values while are not mirrored in the salinity is not extraordinarily high.distribution. This reflects the influence of NADW, which contains that is traced by the relatively large amounts of silicate related to the influence of the Antarctic Bottom Water, which provides high

- $\frac{A_{T} \text{ from dissolution of CaCO}_{3}. \text{ The influence of these high } A_{T} \text{ values is then transported by the ISOW}$ $\frac{A_{T} \text{ from dissolution of CaCO}_{3}. \text{ The influence of these high } A_{T} \text{ values is then transported by the ISOW}$ $\frac{A_{T} \text{ from dissolution of CaCO}_{3}. \text{ The influence of these high } A_{T} \text{ values is then transported by the ISOW}$
- 271 **3.2** Water mass acidification and drivers

272 Trends of pH_{Tis} in each layer and basin are presented in Table 3-and, in Fig. 3 and in Supplementary Fig. S1. 273 The pH_{Tis} has decreased in all layers of the Irminger and Iceland basins during the time period of more than $\frac{320}{2}$ 274 years (19891–2015) that is covered by our the data. The trends are stronger in the Irminger basin due to the 275 presence of younger waters. The rate of OApH decline decreases with depth, except for the DSOW layer that has 276 acidification rates close to those found in the cLSW layer. This indicates that DSOW is a newly formed water 277 mass that has recently been in contact with the atmosphere. Moreover, the acidification rate in the ISOW layer in 278 the Irminger basin is relatively low, which could be related to the increasing importance on this layer of the 279 relatively old NADW in this layer, with the diminutionreduction in-volume of cLSW formation since mid-90s 280 (Lazier et al., 2002; Yashayaev, 2007).

The observed rate of pH_{Tis} decrease in the SPMW layer of the Iceland basin (-0.00126 ± 0.0001 pH units $\cdot yr^{-1}$; 281 282 Table 3, Fig. 3b) is in agreement with that observed at the Iceland Sea time-series (68°N, 12.66°W; Olafsson et al. (2009, 2010)) for the period 1983–2014 (-0.0014 \pm 0.0005 pH units-Bates et al. (2014)). Our rates in the 283 SPMW layer of both basins are slightly lower than those observed at the Subtropical Atlantic time series stations 284 ESTOC (29.04°N, 15.50°W; Santana Casiano et al. (2007). González Dávila et al. (2010)) for the period 1995 285 2014 (0.0018 ± 0.0002 pH units yr⁺; Bates et al. (2014)) and BATS (32°N, 64°W; Bates et al. (2014)) for the 286 period 1983 2014 (0.0017 ± 0.0001 pH units yr⁺; Bates et al. (2014)). However, our rate of pH_{Tis} decrease in 287 the SPMW layer in the Irminger basin $(-0.001\frac{38}{2} \pm 0.0001 \text{ pH units} \cdot \text{yr}^{-1})$ is only half of lower than that observed 288 289 in the sea surface waters of the Irminger Sea time-series (64.3°N, 28°W; Olafsson et al. (2010)) for the period 1983–2014 (-0.0026 \pm 0.0006 pH units-vr⁻¹; Bates et al. (2014)), which is exceptionally high compared to the 290 291 other time series summarized here. Bates et al. (2014) linked the high acidification rate found at the Irminger Sea 292 time-series to the high rate of increase in DIC $(1.62 \pm 0.35 \,\mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{yr}^{-1})$ observed at this site, which is almost twice our rate of increase in DIC ($0.64 \pm 0.07 \mu \text{mol} \cdot \text{kg}^{-1} \cdot \text{yr}^{-1}$, Fig. 5c). This is based on data from only one site, 293 294 further north than our section, and indicates that spatial variations are substantial in this region. Besides, the 295 acidification rates in the SPMW layer of the both basins here reported are in agreement with the rates of -0.0020 \pm 0.0004 pH units yr⁻¹ determined for the North Atlantic subpolar seasonally stratified biome for the period 296 297 1991-2011 (Lauvset et al., 2015). Compared to the Subtropical Atlantic time-series stations, oour rates in the 298 SPMW layer of both basins are slightlyin agreement with-lower than those observed at the Subtropical Atlantic time-series stations-ESTOC (29.04°N, 15.50°W; Santana-Casiano et al. (2007), González-Dávila et al. (2010)) 299 for the period 1995–2014 (-0.0018 ± 0.0002 pH units yr⁻¹; Bates et al. (2014)) and BATS (32°N, 64°W; Bates et al. 300 al. (2014)) for the period 1983–2014 (-0.0017 \pm 0.0001 pH units yr⁻¹; Bates et al. (2014)). Comparinged to with 301 302 the Pacific Ocean, the OA rates in the Iceland and Irminger basins are slightly lower thanin agreement with those 303 reported for the Central North Pacific based on data from the time-series station HOT (22.45°N, 158°W; Dore et al. (2009)) for the period 1988–2014 (-0.0016 \pm 0.0001 pH units vr⁻¹; Bates et al. (2014)), but are in agreement 304 305 withslightly higher than those founddetermined by Wakita et al. (2013) in the winter mixed layer at the Subarctic 306 Western North Pacific (time-series stations K2 and KNOT) for the period 1997–2011 (-0.0010 \pm 0.0004 pH 307 units vr^{-1}). Wakita et al. (2013) attributed the lower than expected pH trends to an increasing A_T trend.

308 Vázquez Rodríguez et al. (2012b) have previously studied the pH changes in the different water masses of the Irminger and Iceland basins, These authors carried out a pH normalization to avoid potential biases due to 309 310 different ventilation stages and rates of each layer, from the different spatial coverage of the evaluated cruises. 311 The normalized pH values (pH_N) for each layer was obtained using multiple linear regressions between the observed mean pH_{2WS25} (pH at seawater scale and 25°C) and the observed mean values of 0, salinity, silicate and 312 mean climatological values of θ , salinity, silicate and AOU compiled in WOA05 313 AOU, referred to the 314 (http://www.node.noaa.gov/OC5/WOA05/pr_woa05.html). This normalization, combined with the lower 315 temporal coverage (1981-2008) and the fact that they evaluated trends in pH at 25°C and not at in situ conditions 316 renders direct comparisons between their and our derived trends difficult.

317 To infer the causes of the acidification trends reported here, we decomposed the pH trends into their individual 318 components as described in Sect. 2.2. The values of each term of $\frac{\partial pH_{Tis}}{\partial var}$ and $\frac{dvar}{dt}$ (where var refers to each of the 319 drivers) described in Sect. 2.2 can be found in the Supplementary Table S2 and in Figs. 4-6, respectively. The 320 results of solving Eq. (2) are presented in Table 3. The sum of the pH changes caused by the individual drivers 321 (in situ temperature, salinity, A_{T} and DIC)i.e., $\left(\frac{dpH_{Tis}}{dt}\right)_{total}$) matches the observed pH trends₇ ($\left(\frac{dpH_{Tis}}{dt}\right)_{obs}$).

322 which renders confidence to the method.

323 The temperature changes (Fig. 4a,b) have generally resulted in small to negligible pH declines (Table 3). Specifically, warming corresponds to a pH decrease of more thanat least 0.00042 pH units yr⁻¹ in the SPMW 324 325 layer of both basins the Iceland basin and in the LSW and DSOW layers of the Irminger basin, while the effect of 326 temperature changes on pH in the other layers is negligible. Temperature driven pH change is larger in the LSW 327 layers in the Irminger than in the Iceland basin. In the case of the uLSW layer, this is possibly explained by the 328 deep convection occurring in the Irminger basin (Pickart et al., 2003; García-Ibáñez et al., 2015; Fröb et al., 329 2016; Piron et al., 2016). In the case of the cLSW layer, the higher pH changes driven by temperature changes in 330 the Irminger basin could be explained by the rapid advection of this water mass from the Labrador Sea to this 331 basin (Yashayaev et al., 2007). Temperature driven pH change in the DSOW layer could be related to the 332 entrainment of LSW into DSOW that takes place downstream of the Greenland-Iceland sills (Read, 2000; Yashayaev and Dickson, 2008). The temperature effect on pH evaluated here is mostly-thermodynamic. The 333 same applies to the salinity effect, which however is small to negligible, reflecting that salinity changes in the 334 335 region (Fig. 4c,d) are insufficiently large to significantly change pH.

336 Overall, tThe A_T has increased in all layersthe Irminger and Iceland basins (Fig. 5a,b), corresponding to 337 increasing pH (Table 3), which counteracts the acidification from the CO_2 absorption. The contribution from A_T to reduce ocean acidification is significant for all the layers, except for ISOW of the Irminger basin and uLSW 338 339 of the Iceland basin (in which where the trend in A_T trends over time is decreasing, but are not significant; Fig. 340 $5_{a,b}$). The similar behaviour of the salinity and A_T trends over time may indicate that the changes in A_T are 341 <u>mainly driven by changes in salinity.</u> The A_T increasing trends observed in <u>the SPMW layer may indicate could</u> 342 be related to the increasing presence of waters of subtropical origin (with higher A_T) as the subpolar gyre was 343 shrinking sincefrom the mid-90s and into the 2000s (e.g., Flatau et al., 2003; Häkkinen and Rhines, 2004; 344 Böning et al., 2006). In the case of the LSW layers, the increase in alkalinity can be explained by the mid-90s cessation of the cLSW formation (Lazier et al., 2002; Yashayaev, 2007), with the consequent salinization (and 345 increase in alkalinity) of this water mass. The signal of the cLSW salinization was then transmitted to the 346 overflow layers due to the entrainment events (Sarafanov et al., 2010) The A_T effect is evident in the ISOW layer 347

348of the Iceland basin, which can be explained by the circulation and mixing of this layer. As ISOW flows349downstream along the Reykjanes Ridge, it mixes with cLSW and NADW (van Aken and de Boer, 1995;350Fogelqvist et al., 2003). The reduced volume of cLSW since mid 90s (Lazier et al., 2002; Yashayaev, 2007) has351increased the importance of NADW (with high A_1 ; Fig. 2h) in the ISOW layer, making the pH decrease of the352ISOW layer of the Iceland basin lower than in the Irminger basin.

353 The DIC increase (Fig. 5c,d) is the main cause of the observed pH decreases (Table 3), and corresponds to pH drops between -0.0008599 and -0.00134205 pH units yr⁻¹ (Table 3). The waters in both the Irminger and Iceland 354 355 basins gained DIC in response to the increase in atmospheric CO₂; the convection processes occurring in these 356 basinsthe former basin (Pickart et al., 2003; Thierry et al., 2008; de Boisséson et al., 2010; García-Ibáñez et al., 357 2015; Fröb et al., 2016; Piron et al., 2016) and in the surrounding ones (i.e., Labrador and Nordic Seas) provide 358 an important pathway for DIC to pass from the surface mixed layer to the intermediate and deep layers. The 359 effect of the DIC increase on pH is generally dominated by the anthropogenic component (Table 3). The 360 exception comes with the cLSW layer of the Irminger basin, where dominates the natural component resulting 361 from the aging of the layer dominates. In general, the Irminger basin All layers have higher Cant increase rates in 362 the Irminger basin than in the Iceland basin layers (Fig. 6a,b), and therefore larger pH declines, presumably a 363 result of the proximity convection in the Irminger basin itself and advection of newly ventilated waters from the Irminger basin to the regions of deep water formationLabrador Sea. The highest Cant increase rates are found in 364 365 the SPMW layer, owing to its direct contact with the atmosphere, and result in the highest strongest rates of pH 366 decrease. The higher pH drops related to C_{init} increase found in the SPMW layer in the Irminger basin compared to those found in the Iceland basin layer, can be related to the differences in the rise in C_{ant} levels in both basins. 367 368 In the Irminger basin, the rise in C_{ant} levels of the SPMW layer correspond to about 857% of the rate expected 369 from a surface ocean maintaining its degree of saturation with the atmospheric CO_2 rise (computed using as 370 reference the measurements of Mauna Loa)globally averaged marine surface annual mean pCO₂ data from the 371 NOAA, ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2 annmean gl.txt), while in the Iceland basin, this rate is 372 about 73% of the expected rate. The lower fraction in the Iceland basin compared to the Irminger basin is a 373 consequence of the inclusion of the aforementioned poorly ventilated thermocline waters in our SPMW layer 374 (Fig. 2e,h). Note than none of the C_{ant} trends of the SPMW layers correspond to 100% of the rate expected from 375 assuming saturation with the atmospheric CO_2 rise. This can be explained by the fact that surface waters CO_2 376 concentration rise lags that of the atmosphere by between two to five years in this region (Biastoch et al., 2007; 377 Jones et al., 2014). We also note that the temperature and A_T changes impact the pH of the SPMW layer, 378 decreasing and increasing it, respectively. This could indicate the increasing presence of warmer and more saline 379 (with higher A_T) waters of subtropical origin, which, because A_T effects dominate (as stated before, the effect of 380 salinity change on pH is negligible), in last instancea net sense partially counteracts the effects of increasing DIC 381 values. Overall this change can be explained as the result of the contraction of the subpolar gyre that took place 382 since mid-90s (e.g., Flatau et al., 2003; Häkkinen and Rhines, 2004; Böning et al., 2006). Wakita et al. (2013) 383 also found lower than expected acidification rates in the surface waters of the Pacific Ocean, which they 384 explained as being the consequence of increasing A_T. Finally, the strong influence of anthropogenic component 385 on the pH decrease of the DSOW layer stands out, and is the main agent of the pH decline in this layer. 386 The pH changes related to C_{nat} changes (Fig. 6c,d) can be interpreted as changes related to ventilation of water

masses and water mass changes (with different AT and DIC). HigherStronger pH decreases related to Cnat

388	changes indicate lack of ventilation and accumulation of DIC from remineralised organic material. This is
389	clearly the case for the cLSW layer, where the observed pH decrease is caused by a combination of the effects of
390	C_{ant} and C_{nat} (Table 3). The greater influence of C_{nat} in the cLSW layer is the result of the aging of this water
391	mass after its last formation event, in the mid-90s (eg., Lazier et al., 2002; Azetsu-Scott et al., 2003; Kieke et al.,
392	2007; Yashayaev, 2007). Similar effect of the C _{nat} changes on pH is observed in the overflow layers of the
393	Irminger basin, which are influenced by the mixing with cLSW (García-Ibáñez et al., 2015). Finally, there is a
394	contrast between the C _{nat} influence on the pH of the uLSW layer in both basins. The inter-annual variability of
395	the uLSW properties attenuates due to mixing over the length and timescales of the transit from the Labrador Sea
396	(Cunningham and Haine, 1995; Paillet et al., 1998), which causes the inter-annual variability in the C _{nat} values of
397	the uLSW layer in the Iceland basin to be smoother than in the Irminger basin (Fig. 6c,d). Therefore, the lower
398	inter-annual variability in the C _{nat} values of the uLSW layer in the Iceland basin promotes better detectability of
399	the ventilation of the uLSW layer, whose effects offset up to 60% the effects of acidification on the uLSW layer
400	of the Iceland basinCnat also contributes to pH changes in the ISOW layer of the Iceland basin, which is related
401	to the increasing influence of the relatively old NADW over time due to the decreasing contribution of LSW (Sy
402	et al., 1997; Yashayaev, 2007; Sarafanov et al., 2010; García Ibáñez et al., 2015).
403	Vázquez-Rodríguez et al. (2012b) have previously studied the pH changes in the different water masses of the
404	Irminger and Iceland basins. These authors carried out a pH normalization to avoid potential biases due to
405	different ventilation stages and rates of each layer, from the different spatial coverage of the evaluated cruises.
406	The normalized pH values (pH _N) for each layer was obtained using multiple linear regressions between the
407	observed mean pH _{SWS25} (pH at seawater scale and 25°C) and the observed mean values of θ , salinity, silicate and
408	AOU, referred to the mean climatological values of θ , salinity, silicate and AOU compiled in WOA05
409	(http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html). This normalization, combined with the
410	lowerdifferent temporal coverage (1981-2008) and the fact that they evaluated trends in pH at 25°C and not at in
411	situ conditions, causes the rates reported by Vazquez-Rodriguez et al. (2012b) differ from those obtained in the
412	present work-renders direct comparisons between their and our derived trends difficult. The pH _N trends reported
413	for the SPMW and uLSW layers of the Irminger basin and for the ISOW layer of the Iceland basin are very
414	similar to our pH _{Tis} trends for these layers. However, the pH _N trends reported by Vazquez-Rodriguez et al.
415	(2012b) for the cLSW layer in both basins and for the ISOW layer in the Irminger basin are significantly
416	different from our pH _{Tis} trends for these layers, but are very similar to pH changes derived from C _{ant} changes
417	$(\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt} \text{ in Table 3}). \text{ In the case of the DSOW layer, the pH}_{N} \text{ trend is also in agreement with } \frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}$
418	trends. This suggests that the normalization carried out by Vazquez-Rodriguez et al. (2012b) could remove some
419	of the impact of the natural component (represented here by C _{nat}) over pH changes, essentially due to the use of
420	AOU in the normalization.

421 4 CONCLUSIONS

The progressive acidification of the North Atlantic waters has been assessed from direct observations obtained over the last three decades 25 years (19891–2015), with the greatest pH decreases observed in surface and intermediate waters. By separatingFrom the study of the main drivers of the observed pH change into its main drivers,changes we corroborate conclude that the observed pH decreases are mainly a consequence of the oceanic 426 Cant uptake-and in. In addition we find that they have been partially offset by AT increases. However Thus, while 427 the C_{ant} concentration of the upper layer roughly keeps up with that expected from rising atmospheric CO₂, the 428 pH decreases at a lower rate than expected from C_{ant} increase. The increasing arrival of saltysaline and alkaline 429 subtropical waters transported by the NAC to the study region related to the contraction of the subpolar gyre 430 since mid-90's buffers the acidification caused by the Cant increase in the upper layer. The acidification rates in 431 intermediate waters are similar to those in the surface waters, and are caused by a combination of anthropogenic 432 and non-anthropogenic components. The acidification of cLSW due to the Cant uptake is reinforced by the aging 433 of this water mass from the end of the 1990s onwards. The pH of the deep waters of the Irminger basin, DSOW, 434 has clearly decreased in response to anthropogenic forcing. We also observeinfer that water mass warming 435 contributes between 132 and 1825% to the pH decrease of the upper and intermediate waters of the Irminger 436 basin, and 3410% to the pH decrease of the upper waters of the Iceland basin.

437 Author Contributions

438 All authors contributed extensively to the work presented in this paper. M.I.G.-I., A.F.R., H.M., A.O. and 439 F.F.P. designed the research. M.I.G.-I., P.Z., F.F., L.I.C., A.F.R., H.M., A.O. and F.F.P. analysed the physical 440 and chemical data. M.I.G.-I. and P.Z. developed the code for processing the data. M.I.G.-I. and F.F.P. 441 determined the anthropogenic CO_2 concentrations, average layer properties and rates, and estimated the 442 uncertainties. M.I.G.-I. wrote the manuscript and prepared all figures, with contributions from all co-authors.

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455 **References**

456 Álvarez, M., Ríos, A.F., Pérez, F.F., Bryden, H.L., and Rosón, G.: Transports and budgets of total inorganic
457 carbon in the subpolar and temperate North Atlantic, Glob. Biogeochem. Cycles, 17, 1002,
458 doi:10.1029/2002GB001881, 2003.

- 459 Anderson, L.G. and Olsen, A.: Air-sea flux of anthropogenic carbon dioxide in the North Atlantic, Geophys.
- 460 Res. Lett., 29, 1835, doi: 10.1029/2002GL014820, 2002.

- 461 Azetsu-Scott, K., Jones, E.P., Yashayaev, I., and Gershey, R.M.: Time series study of CFC concentrations in the
- 462 Labrador Sea during deep and shallow convection regimes (1991–2000), J. Geophys. Res., 108, 3354,
- 463 doi:10.1029/2002JC001317, 2003.
- 464 Bates, N., Astor, Y., Church, M., Currie, K., Dore, J., Gonazález-Dávila, M., Lorenzoni, L., Muller-Karger, F.,
- 465 Olafsson, J., and Santa-Casiano, M.: A Time-Series View of Changing Ocean Chemistry Due to Ocean Uptake
- 466 of Anthropogenic CO₂ and Ocean Acidification, Oceanography, 27, 126–141, doi:10.5670/oceanog.2014.16,
- 467 2014.
- Bates, N.R., Best, M.H.P., Neely, K., Garley, R., Dickson, A.G., and Johnson, R.J.: Detecting anthropogenic
 carbon dioxide uptake and ocean acidification in the North Atlantic Ocean, Biogeosciences, 9, 2509–2522,
- 470 doi:10.5194/bg-9-2509-2012, 2012.
- 471 Benson, B.B. and Krause, D.: The concentration and isotopic fractionation of oxygen dissolved in freshwater and
- 472 seawater in equilibrium with the atmosphere, Limnol. Oceanogr., 29, 620–632, doi:10.4319/lo.1984.29.3.0620,
 473 1984.
- 474 Bersch, M., Meincke, J., and Sy, A.: Interannual thermohaline changes in the northern North Atlantic 1991-
- 475 1996, Deep Sea Res. Part II Top. Stud. Oceanogr., 46, 55–75, doi:10.1016/S0967-0645(98)00114-3, 1999.
- 476 Biastoch, A., Völker, C., and Böning, C.W.: Uptake and spreading of anthropogenic trace gases in an eddy-
- 477 permitting model of the Atlantic Ocean, J. Geophys. Res., 112, C09017, doi:10.1029/2006JC003966, 2007.
- Böning, C.W., Scheinert, M., Dengg, J., Biastoch, A., and Funk, A.: Decadal variability of subpolar gyre
 transport and its reverberation in the North Atlantic overturning, Geophys. Res. Lett., 33, L21S01,
- 480 doi:10.1029/2006GL026906, 2006.
- 481 Bradshaw, A., Brewer, P., Shafer, D., and Williams, R.: Measurements of total carbon dioxide and alkalinity by
- 482 potentiometric titration in the GEOSECS program, Earth Planet. Sci. Lett., 55, 99–115, doi:10.1016/0012-
- 483 <u>821X(81)90090 X, 1981.</u>
- Brambilla, E. and Talley, L.D.: Subpolar Mode Water in the northeastern Atlantic: 1. Averaged properties and
 mean circulation, J. Geophys. Res., 113, C04025, doi:10.1029/2006JC004062, 2008.
- 486 Brewer, P.G., Takahashi, T., and Williams, R.T.: Transient tracers in the ocean (TTO) Hydrographic data and
- 487 carbon dioxide systems with revised carbon chemistry data, NDP 004/R, Carbon Dioxide Information Center,
- 488 Oak Ridge National Laboratory, Oak Ridge, TN, 28 pp., doi:10.2172/538035, 1986.
- 489 Broecker, W.S.: "NO" a conservative water mass tracer, Earth and Planetary Science Letters, 23, 8761–8776,
 490 doi:10.1016/0012-821X(74)90036-3, 1974.
- 491 Caldeira, K. and Wickett, M.E.: Oceanography: Anthropogenic carbon and ocean pH, Nature, 425, 365–365,
 492 doi:10.1038/425365a, 2003.
- 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.
- 495 Carter, B.R., Radich, J.A., Doyle, H.L., and Dickson, A.G.: An automated system for spectrophotometric
- 496 seawater pH measurements, Limnol. Oceanogr. Methods, 11, 16–27, doi:10.4319/lom.2013.11.16, 2013.
- 497 Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A., DeFries, R., Galloway, J.,
- 498 Heimann, M., Jones, C., Le Quéré, C., Myneni, R.B., Piao, S., and Thornton, P.: Carbon and other
- 499 biogeochemical cycles, in: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I
- 500 to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., Qin, D.,

- 501 Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex V., and Midgley, P.M. (eds.)],
- 502 Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. 465-570, 2013.
- 503 Clayton, T.D. and Byrne, R.H.: Spectrophotometric seawater pH measurements: total hydrogen ion
- 504 concentration scale calibration of m-cresol purple and at-sea results, Deep Sea Res. Part I: Oceanogr. Res. Pap.,
- 505 40, 2115–2129, doi:10.1016/0967-0637(93)90048-8, 1993.
- 506 Cunningham, S.A. and Haine, T.W.N.: Labrador Sea Water in the eastern North Atlantic. Part II: mixing 507 dynamics and the advective-diffusive balance, Journal of Physical Oceanography, 14, 103-127.
- 508 doi:10.1175/1520-0485(1995) 025<0666:LSWITE>2.0.CO;2, 1995.
- 509 de Boisséson, E., Thierry, V., Mercier, H., and Caniaux, G.: Mixed layer heat budget in the Iceland Basin from
- 510 Argo, J. Geophys. Res. Oceans, 115, C10055, doi:10.1029/2010JC006283, 2010.
- 511 Desbruyères, D., Thierry, V., and Mercier, H.: Simulated decadal variability of the meridional overturning
- 512 circulation across the A25-Ovide section, J. Geophys. Res. Oceans, 118, 462–475, doi:10.1029/2012JC008342,
- 513 2013.
- 514 DeVries, T.: The oceanic anthropogenic CO₂ sink: Storage, air-sea fluxes, and transports over the industrial era,

515 Glob. Biogeochem. Cycles, 28, 631-647, doi:10.1002/2013GB004739, 2014.

- 516 Dickson, A.G.: The measurement of sea water pH, Mar. Chem., 44, 131-142, doi:10.1016/0304-4203(93)90198-517 W, 1993a
- 518
- Dickson, A.G.: pH buffers for sea water media based on the total hydrogen ion concentration scale, Deep Sea 519 Res. Part I: Oceanogr. Res. Pap., 40, 107-118, doi:10.1016/0967-0637(93)90055-8, 1993b.
- 520 Dickson, A. and Goyet, C.: Handbook of methods for the analysis of the various parameters of the carbon
- 521 dioxide system in sea water. Version 2, Oak Ridge National Laboratory, Oak Ridge, TN, 198 pp., 522 doi:10.2172/10107773, 1994.
- 523 Dickson, A.G., Sabine, C.L., and Christian, J.R.: Guide to best practices for ocean CO₂ measurements, PICES
- 524 Spec. Publ., 3, North Pacific Marine Science Organization Sidney, British Columbia, 191 pp., 2007.
- 525 Dickson, A. and Millero, F.: A comparison of the equilibrium constants for the dissociation of carbonic acid in
- 526 seawater media, Deep-Sea Res., 34, 1733-1743, doi:10.1016/0198-0149(87)90021-5, 1987.
- 527 Doney, S.C., Fabry, V.J., Feely, R.A., and Kleypas, J.A.: Ocean acidification: the other CO₂ problem, Annu.
- 528 Rev. Mar. Sci., 1, 169–192, doi:10.1146/annurev.marine.010908.163834, 2009.
- 529 Dore, J.E., Lukas, R., Sadler, D.W., Church, M.J., and Karl, D.M.: Physical and biogeochemical modulation of
- ocean acidification in the central North Pacific, Proc. Natl. Acad. Sci., 106, 12235-12240, 530
- 531 doi:10.1073/pnas.0906044106, 2009.
- 532 Eakins, B.W. and Sharman, G.F.: Volumes of the World's Oceans from ETOPO1, NOAA National Geophysical
- 533 Data Center, Boulder, CO, 2010.
- 534 Feely, R.A., Doney, S.C., and Cooley, S.R.: Ocean acidification: Present and future changes in a high-CO₂
- 535 world, Oceanography, 22, 36-47, doi:10.5670/oceanog.2009.95, 2009.
- 536 Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J., and Millero, F.J.: Impact of
- 537 Anthropogenic CO₂ on the CaCO₃ System in the Oceans, Science, 305, 362–366, doi:10.1126/science.1097329,
- 538 2004.
- 539 Flatau, M.K., Talley, L., and Niiler, P.P.: The North Atlantic Oscillation, Surface Current Velocities, and SST
- 540 Changes in the Subpolar North Atlantic, J. Clim., 16, 2355–2369, doi:10.1175/2787.1, 2003.

- 541 Fogelqvist, E., Blindheim, J., Tanhua, T., Østerhus, S., Buch, E., and Rey, F.: Greenland Scotland overflow
- 542 studied by hydro chemical multivariate analysis, Deep Sea Res. Part I: Oceanogr. Res. Pap., 50, 73-102,
- 543 doi:10.1016/S0967-0637(02)00131-0, 2003.
- 544 Fröb, F., Olsen, A., Våge, K., Moore, K., Yashayaev, I., Jeannson, E., and Rajasakaren, B.: Record deep
- 545 convection in the Irminger Sea in winter 2014-15, OSM, New Orleans, Louisiana, USA, 21-16 February 2016, 546 HE11A-02, 2016.
- 547 García-Ibáñez, M.I., Pardo, P.C., Carracedo, L.I., Mercier, H., Lherminier, P., Ríos, A.F., and Pérez, F.F.:
- 548 Structure, transports and transformations of the water masses in the Atlantic Subpolar Gyre, Prog. Oceanogr.,
- 549 135, 18-36, doi:10.1016/j.pocean.2015.03.009, 2015.
- 550 Gattuso, J. P., Brewer, P.G., Hoegh Guldberg, O., Kleypas, J.A., Pörtner, H. O., and Schmidt, D.N.: Cross-
- chapter box on ocean acidification, in: IPCC, 2014: Climate Change 2014: Impacts, Adaptation, and 551
- 552 Vulnerability. Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Field, C.B., Barros, V.R., Dokken, D.J., Mach, K.J.,
- 553
- 554 Mastrandrea, M.D., Bilir, T.E., Chatterjee, M., Ebi, K.L., Estrada, Y.O., Genova, R.C., Girma, B., Kissel, E.S.,
- 555 Levy, A.N., MacCracken, S., Mastrandrea, P.R., and White, L.L. (eds.)], Cambridge University Press,
- 556 Cambridge, United Kingdom and New York, NY, USA, 129-13, 2014.
- 557 Gehlen, M., Gruber, N., Gangstø, R., Bopp, L., and Oschlies, A.: Biogeochemical consequences of ocean 558 acidification and feedbacks to the earth system, in: Ocean Acidification, Vol. 1 [Gattuso, J.-P. and Hansson, L. 559 (eds.)], Oxford University Press, 230-248, 2011.
- 560 González-Dávila, M., Santana-Casiano, J.M., Rueda, M.J., and Llinás, O.: The water column distribution of
- 561 carbonate system variables at the ESTOC site from 1995 to 2004, Biogeosciences, 7, 3067-3081,
- 562 doi:10.5194/bg-7-3067-2010, 2010.
- 563 Gourcuff, C., Lherminier, P., Mercier, H., and Le Traon, P.Y.: Altimetry Combined with Hydrography for Ocean
- 564 Transport Estimation, J. Atmospheric Ocean. Technol., 28, 1324–1337, doi:10.1175/2011JTECH0818.1, 2011.
- 565 Gruber, N., Sarmiento, J.L., and Stocker, T.F.: An improved method for detecting anthropogenic CO₂ in the oceans, Global Biogeochem. Cycles, 10(4), 809-837, doi:10.1029/96GB01608, 1996. 566
- 567 Guallart, E.F., Fajar, N.M., Padín, X.A., Vázquez-Rodríguez, M., Calvo, E., Ríos, A.F., Hernández-Guerra, A.,
- 568 Pelejero, C., and Pérez, F.F.: Ocean acidification along the 24.5°N section in the subtropical North Atlantic, 569 Geophys. Res. Lett., 42, 2014GL062971, doi:10.1002/2014GL062971, 2015.
- 570 Häkkinen, S. and Rhines, P.B.: Decline of subpolar North Atlantic circulation during the 1990s, Science, 304,
- 571 555-559, doi:10.1126/science.1094917, 2004.
- 572 Johnson, K.M., Wills, K.D., Butler, D.B., Johnson, W.K., and Wong, C.S.: Coulometric total carbon dioxide
- 573 analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric 574 detector, Mar. Chem., 44, 167-187, doi:10.1016/0304-4203(93)90201-X, 1993.
- 575 Jones, D.C., Ito, T., Takano, Y., and Hsu, W.-C.: Spatial and seasonal variability of the air-sea equilibration 576 timescale of carbon dioxide, Glob. Biogeochem. Cycles, 28, 1163-1178, doi:10.1002/2014GB004813, 2014.
- 577 Khatiwala, S., Tanhua, T., Mikaloff Fletcher, S., Gerber, M., Doney, S.C., Graven, H.D., Gruber, N., McKinley,
- 578 G.A., Murata, A., Ríos, A.F., and Sabine, C.L.: Global ocean storage of anthropogenic carbon, Biogeosciences,
- 579 10, 2169-2191, doi:10.5194/bg-10-2169-2013, 2013.

- Kieke, D., Rhein, M., Stramma, L., Smethie, W.M., Bullister, J.L., and LeBel, D.A.: Changes in the pool of
 Labrador Sea Water in the subpolar North Atlantic, Geophys. Res. Lett., 34, L06605,
 doi:10.1029/2006GL028959, 2007.
- 583 Koltermann, K.P., Pfannkuche, O., and Meincke, J.: JGOFS, OMEX and WOCE in the North Atlantic 1994,
- 584 cruise no. 30: 7 September-22 December 1994, Meteor-Berichte, 96-3, Universität Hamburg, 148 pp., 1996.
- 585 Langdon, C., Takahashi, T., Sweeney, C., Chipman, D., Goddard, J., Marubini, F., Aceves, H., Barnett, H., and
- 586 Atkinson, M.J.: Effect of calcium carbonate saturation state on the calcification rate of an experimental coral
- 587 reef, Glob. Biogeochem. Cycles, 14, 639–654, doi:10.1029/1999GB001195, 2000.
- Lauvset, S.K., Gruber, N., Landschützer, P., Olsen, A., and Tjiputra, J.: Trends and drivers in global surface
 ocean pH over the past 3 decades, Biogeosciences, 12, 1285-1298, doi:10.5194/bg-12-1285-2015, 2015.
- 590 Lazier, J., Hendry, R., Clarke, A., Yashayaev, I., and Rhines, P.: Convection and restratification in the Labrador
- Sea, 1990–2000, Deep Sea Res. Part I: Oceanogr. Res. Pap., 49, 1819–1835, doi:10.1016/S0967-0637(02)00064X, 2002.
- 593 Le Quéré, C., Moriarty, R., Andrew, R.M., Canadell, J.G., Sitch, S., Korsbakken, J.I., Friedlingstein, P., Peters,
- 594 G.P., Andres, R.J., Boden, T.A., Houghton, R.A., House, J.I., Keeling, R.F., Tans, P., Arneth, A., Bakker,
- 595 D.C.E., Barbero, L., Bopp, L., Chang, J., Chevallier, F., Chini, L.P., Ciais, P., Fader, M., Feely, R.A., Gkritzalis,
- 596 T., Harris, I., Hauck, J., Ilyina, T., Jain, A.K., Kato, E., Kitidis, V., Klein Goldewijk, K., Koven, C.,
- 597 Landschützer, P., Lauvset, S.K., Lefèvre, N., Lenton, A., Lima, I.D., Metzl, N., Millero, F., Munro, D.R.,
- 598 Murata, A., Nabel, J.E.M.S., Nakaoka, S., Nojiri, Y., O'Brien, K., Olsen, A., Ono, T., Pérez, F.F., Pfeil, B.,
- 599 Pierrot, D., Poulter, B., Rehder, G., Rödenbeck, C., Saito, S., Schuster, U., Schwinger, J., Séférian, R., Steinhoff,
- 600 T., Stocker, B.D., Sutton, A.J., Takahashi, T., Tilbrook, B., van der Laan-Luijkx, I.T., van der Werf, G.R., van
- Heuven, S., Vandemark, D., Viovy, N., Wiltshire, A., Zaehle, S., and Zeng, N.: Global Carbon Budget 2015,
- 602 Earth Syst. Sci. Data, 7, 349–396, doi:10.5194/essd-7-349-2015, 2015.
- 603 Lherminier, P., Mercier, H., Gourcuff, C., Alvarez, M., Bacon, S., and Kermabon, C.: Transports across the 2002
- 604 Greenland-Portugal Ovide section and comparison with 1997, J. Geophys. Res., 112, C07003, 605 doi:10.1029/2006JC003716, 2007.
- 606 Lherminier, P., Mercier, H., Huck, T., Gourcuff, C., Perez, F.F., Morin, P., Sarafanov, A., and Falina, A.: The
- 607 Atlantic Meridional Overturning Circulation and the subpolar gyre observed at the A25-OVIDE section in June
- 608 2002 and 2004, Deep Sea Res. Part I: Oceanogr. Res. Pap., 57, 1374–1391, doi:10.1016/j.dsr.2010.07.009, 2010.
- 609 Liu, X., Patsavas, M.C., and Byrne, R.H.: Purification and Characterization of meta-Cresol Purple for
- 610 Spectrophotometric Seawater pH Measurements, Environ. Sci. Technol., 45, 4862–4868, doi:10.1021/es200665d 611 , 2011.
- 612 Maier-Reimer, E. and Hasselmann, K.: Transport and storage of CO_2 in the ocean—an inorganic ocean-613 circulation carbon cycle model, Clim. Dyn., 2, 63–90, doi:10.1007/BF01054491, 1987.
- Matear, R.J. and Lenton, A.: Quantifying the impact of ocean acidification on our future climate,
 Biogeosciences, 11, 3965–3983, doi:10.5194/bg-11-3965-2014, 2014.
- 616 Mehrbach, C., Culberson, C.H., Hawley, J.E., and Pytkowicz, R.M.: Measurement of the apparent dissociation
- 617 constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr., 18, 897-907,
- 618 doi:10.4319/lo.1973.18.6.0897, 1973.

- 619 Meincke, J. and Becker, G.: WOCE-NORD, Cruise No. 18, 2 September-26 September 1991. Nordsee, cruise
- 620 No. 19, 30 September-12 October 1991. METEOR-Berichte 93-1, Univ. Hambg., 105 pp., 1993.
- 621 Mercier, H., Lherminier, P., Sarafanov, A., Gaillard, F., Daniault, N., Desbruyères, D., Falina, A., Ferron, B.,
- 622 Gourcuff, C., and Huck, T.: Variability of the meridional overturning circulation at the Greenland–Portugal
- 623 OVIDE section from 1993 to 2010, Prog. Oceanogr., 132, 250–261, doi:10.1016/j.pocean.2013.11.001, 2015.
- 624 Millero, F.J., Zhang, J.Z., Lee, K., and Campbell, D.M.: Titration alkalinity of seawater, Mar. Chem., 44, 153–
- 625 165, doi:10.1016/0304-4203(93)90200-8, 1993.
- 626 Mintrop, L., Pérez, F.F., González-Dávila, M., Santana-Casiano, J.M., and Körtzinger, A.: Alkalinity
- determination by potentiometry: Intercalibration using three different methods, Cienc. Mar., 26, 23–37,
 doi:10.7773/cm.v26i1.573, 2000.
- 629 Olafsson, J., Olafsdottir, S.R., Benoit-Cattin, A., Danielsen, M., Arnarson, T.S., and Takahashi, T.: Rate of
- Iceland Sea acidification from time series measurements, Biogeosciences, 6, 2661–2668, doi:10.5194/bg-62661-2009, 2009.
- 632 Olafsson, J., Olafsdottir, S.R., Benoit-Cattin, A., Takahashi, T.: The Irminger Sea and the Iceland Sea time series
- 633 measurements of sea water carbon and nutrient chemistry 1983-2008, Earth Syst. Sci. Data, 2, 99-104,
- 634 doi:10.5194/essd-2-99-2010, 2010.
- 635 Olsen, A., Abdirahman, O.M., Bellerby, R.G., Johannessen, T., Ninnemann, U.S., Brown, K.R., Olsson, K.A.,
- 636 Olafsson, J., Nondal, G., Kivimäe, C., Kringstad, S., Neill, C., Olafsdottir, S.: Magnitude and Origin of the 637 Anthropogenic CO_2 Increase and the ¹³C Suess Effect in the Nordic Seas since 1981, Glob. Biogeochem. Cycles,
- 638 20, GB3027, doi:10.1029/2005GB002669, 2006.
- 639 Olsen, A., Key, R.M., Heuven, S. van, Lauvset, S.K., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T.,
- 640 Hoppema, M., Jutterström, S., Steinfeldt, R., Jeansson, E., Ishii, M., Pérez, F.F., and Suzuki, T.: An internally
- 641 consistent data product for the world ocean: the Global Ocean Data Analysis Project, version 2 (GLODAPv2),
- Earth Syst. Sci. Data Discuss., doi:10.5194/essd-2015-42, in review, 2016.
- 643 Ono, T., Watanabe, S., Okuda, K., and Fukasawa, M.: Distribution of total carbonate and related properties in
- 644 the North Pacific along 30°N, J. Geophys. Res. Oceans, 103, 30873–30883, doi:10.1029/1998JC900018, 1998.
- 645 Orr, J.C.: Recent and future changes in ocean carbonate chemistry, in: Ocean Acidification, Vol. 1, [Gattuso, J.-
- 646 P. and Hansson, L. (eds.)], Oxford University Press, 41–66, 2011.
- 647 Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A.,
- 648 Joos, F., Key, R.M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.G., Plattner,
- 649 G. K., Rodgers, K.B., Sabine, C.L., Sarmiento, J.L., Schlitzer, R., Slater, R.D., Totterdell, I.J., Weirig, M.F.,
- 650 Yamanaka, Y., and Yool, A.: Anthropogenic ocean acidification over the twenty first century and its impact on
- 651 calcifying organisms, Nature, 437, 681–686, doi:10.1038/nature04095, 2005.
- Paillet, J., Arhan, M., and McCartney, M.S.: Spreading of Labrador Sea Water in the eastern North Atlantic,
 Journal of Geophysical Research 103 (C5), 10223-10239, doi:10.1029/98JC00262, 1998.
- Pérez, F.F. and Fraga, F.: A precise and rapid analytical procedure for alkalinity determination, Mar. Chem., 21,
 169–182, doi:10.1016/0304-4203(87)90037-5, 1987.
- 656 Pérez, F.F., Mercier, H., Vázquez-Rodríguez, M., Lherminier, P., Velo, A., Pardo, P.C., Rosón, G., and Ríos,
- A.F.: Atlantic Ocean CO₂ uptake reduced by weakening of the meridional overturning circulation, Nat. Geosci.,
- 658 6, 146–152, doi:10.1038/ngeo1680, 2013.

- 659 Pérez, F.F., Vázquez-Rodríguez, M., Louarn, E., Padín, X.A., Mercier, H., and Ríos, A.F.: Temporal variability
- of the anthropogenic CO₂ storage in the Irminger Sea, Biogeosciences, 5, 1669–1679, doi:10.5194/bg-5-1669-
- 661 2008, 2008.
- Pérez, F.F., Vázquez-Rodríguez, M., Mercier, H., Velo, A., Lherminier, P., and Ríos, A.F.: Trends of
 anthropogenic CO₂ storage in North Atlantic water masses, Biogeosciences, 7, 1789–1807, doi:10.5194/bg-7-
- 664 1789-2010, 2010.
- Pickart, R.S., Straneo, F., and Moore, G.K.: Is Labrador Sea Water formed in the Irminger basin?, Deep Sea Res.
 Part I: Oceanogr. Res. Pap., 50, 23–52, doi:10.1016/S0967-0637(02)00134-6, 2003.
- Piron, A., Thierry, V., Mercier, H., and Caniaux, G.: Argo float observations of basin-scale deep convection in
 the Irminger sea during winter 2011-2012, Deep Sea Res. Part I: Oceanogr. Res. Pap., 109, 76–90,
 doi:10.1016/j.dsr.2015.12.012, 2016.
- 670 Pörtner, H.O., Langenbuch, M., and Reipschläger, A.: Biological Impact of Elevated Ocean CO₂ Concentrations:
- 671 Lessons from Animal Physiology and Earth History, J. Oceanogr., 60, 705–718, doi:10.1007/s10872-004-5763672 0, 2004.
- 673 Quay, P., Sonnerup, R., Stutsman, J., Maurer, J., Körtzinger, A., Padin, X.A., and Robinson, C.: Anthropogenic
- 674 CO₂-accumulation rates in the North Atlantic Ocean from changes in the ¹³C/¹²C of dissolved inorganic carbon,
 675 Glob. Biogeochem. Cycles, 21, GB1009, doi:10.1029/2006GB002761, 2007.
- Raven, J., Caldeira, K., Elderfield, H., Hoegh-Guldberg, O., Liss, P., Riebesell, U., Shepherd, J., Turley, C., and
 Watson, A.: Ocean acidification due to increasing atmospheric carbon dioxide, R. Soc. Lond. Document No.
- 678 12/05, The Royal Society, London, 2005.
- 679 <u>Read, J.F.: CONVEX-91: water masses and circulation of the Northeast Atlantic subpolar gyre, Progress in</u>
 680 <u>Oceanography, 48 (4), 461–510, doi:10.1016/S0079-6611(01)00011-8, 2000.</u>
- 681 Rhein, M., Fischer, J., Smethie, W.M., Smythe-Wright, D., Weiss, R.F., Mertens, C., Min, D.-H., Fleischmann,
- 682 U., and Putzka, A.: Labrador Sea Water: Pathways, CFC inventory, and formation rates, J. Phys. Oceanogr., 32,
- 683 648–665, doi:10.1175/1520-0485(2002)032<0648:LSWPCI>2.0.CO;2, 2002.
- Riebesell, U., Zondervan, I., Rost, B., Tortell, P.D., Zeebe, R.E., and Morel, F.M.M.: Reduced calcification of
- marine plankton in response to increased atmospheric CO₂, Nature, 407, 364–367, doi:10.1038/35030078, 2000.
- 686 Ríos, A.F., Álvarez-Salgado, X.A., Pérez, F.F., Bingler, L.S., Arístegui, J., and Mémery, L.: Carbon dioxide
- along WOCE line A14: Water masses characterization and anthropogenic entry, J. Geophys. Res. Oceans, 108,
- 688 3123, doi:10.1029/2000JC000366, 2003.
- 689 Ríos, A.F., Resplandy, L., García-Ibáñez, M.I., Fajar, N.M., Velo, A., Padin, X.A., Wanninkhof, R., Steinfeldt,
- 690 R., Rosón, G., and Pérez, F.F.: Decadal acidification in the water masses of the Atlantic Ocean, Proc. Natl. Acad.
- 691 Sci., 112, 9950–9955, doi:10.1073/pnas.1504613112, 2015.
- 692 Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace,
- 693 D.W.R., Tilbrook, B., Millero, F.J., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A.F.: The Oceanic Sink for
- 694 Anthropogenic CO₂, Science, 305, 367–371, doi:10.1126/science.1097403, 2004.
- 695 Santana-Casiano, J.M., González-Dávila, M., Rueda, M.-J., Llinás, O., and González-Dávila, E.-F.: The
- 696 interannual variability of oceanic CO₂ parameters in the northeast Atlantic subtropical gyre at the ESTOC site,
- 697 Glob. Biogeochem. Cycles, 21, GB1015, doi:10.1029/2006GB002788., 2007.

- 698 Sarafanov, A., Falina, A., Mercier, H., Sokov, A., Lherminier, P., Gourcuff, C., Gladyshev, S., Gaillard, F., and
- Daniault, N.: Mean full-depth summer circulation and transports at the northern periphery of the Atlantic Ocean
- 700 in the 2000s, J. Geophys. Res., 117, C01014, doi:10.1029/2011JC007572, 2012.
- 701 Sarafanov, A., Falina, A., Sokov, A., and Demidov, A.: Intense warming and salinification of intermediate
- waters of southern origin in the eastern subpolar North Atlantic in the 1990s to mid-2000s, J. Geophys. Res.
 Oceans, 113, C12022, doi:10.1029/2008JC004975, 2008.
- 704 Sarafanov, A., Mercier, H., Falina, A., Sokov, A., and Lherminier, P.: Cessation and partial reversal of deep
- 705 water freshening in the northern North Atlantic: observation-based estimates and attribution, Tellus A, 62, 80–
- 706 90, doi:10.1111/j.1600-0870.2009.00418.x, 2010.
- 707 Sarmiento, J.L., Orr, J.C., and Siegenthaler, U.: A perturbation simulation of CO₂ uptake in an ocean general
- 708 circulation model, J. Geophys. Res. Oceans, 97, 3621–3645, doi:10.1029/91JC02849, 1992.
- 709 Steinfeldt, R., Rhein, M., Bullister, J.L., and Tanhua, T.: Inventory changes in anthropogenic carbon from 1997–
- 710 2003 in the Atlantic Ocean between 20°S and 65°N, Glob. Biogeochem. Cycles, 23, GB3010,
- 711 doi:10.1029/2008GB003311, 2009.
- 712 Stoll, M.H.C., van Aken, H.M., de Baar, H.J.W., and Kraak, M.: Carbon dioxide characteristics of water masses
- 713 in the northern North Atlantic Ocean, Mar. Chem., 55, 217–232, doi:10.1016/S0304-4203(96)00058-8, 1996.
- 714 Sy, A., Rhein, M., Lazier, J.R.N., Koltermann, K.P., Meincke, J., Putzka, A., and Bersch, M.: Surprisingly rapid
- spreading of newly formed intermediate waters across the North Atlantic Ocean, Nature, 386, 675–679,
 doi:10.1038/386675a0, 1997.
- 717 Takahashi, T. and Brewer, P.: Hydrographic and chemistry data for the TTO/NAS expedition, April October,
- 718 1981: Revised carbon chemistry data Rep. NDP004, Carbon Dioxide Inf. Anal. Cent., Oak Ridge, TN, 1986.
- 719 Tanhua, T. and Wallace, D.W.R.: Consistency of TTO-NAS inorganic carbon data with modern measurements,
- 720 Geophys. Res. Lett., 32, L14618, doi:10.1029/2005GL023248, 2005.
- Thierry, V., de Boisséson, E., and Mercier, H.: Interannual variability of the Subpolar Mode Water properties
 over the Reykjanes Ridge during 1990–2006, J. Geophys. Res. Oceans, 113, C04016,
 doi:10.1029/2007JC004443, 2008.
- 724 <u>Uppström, L.R.: Boron/chlorinity ratio of deep-sea water from the Pacific Ocean, Deep-Sea Res., 21, 161-162,</u>
 725 doi:10.1016/0011-7471(74)90074-6, 1974.
- 726 van Aken, H.M. and de Boer, C.J.: On the synoptic hydrography of intermediate and deep water masses in the
- 727 Iceland Basin, Deep Sea Res. Part I: Oceanogr. Res. Pap., 42, 165–189, doi:10.1016/0967-0637(94)00042-Q,
 728 1995.
- 729 Vázquez-Rodríguez, M., Padin, X.A., Ríos, A.F., Bellerby, R.G.J., and Pérez, F.F.: An upgraded carbon-based
- 730 method to estimate the anthropogenic fraction of dissolved CO_2 in the Atlantic Ocean, Biogeosciences Discuss.,
- 731 6, 4527–4571, doi:10.5194/bgd-6-4527-2009, 2009a.
- 732 Vázquez-Rodríguez, M., Touratier, F., Lo Monaco, C., Waugh, D.W., Padin, X.A., Bellerby, R.G.J., Goyet, C.,
- Metzl, N., Ríos, A.F., and Pérez, F.F.: Anthropogenic carbon distributions in the Atlantic Ocean: data-based
 estimates from the Arctic to the Antarctic, Biogeosciences, 6, 439–451, doi:10.5194/bg-6-439-2009, 2009b.
- 735 Vázquez-Rodríguez, M., Padin, X.A., Pardo, P.C., Ríos, A.F., and Pérez, F.F.: The subsurface layer reference to
- rac calculate preformed alkalinity and air-sea CO₂ disequilibrium in the Atlantic Ocean, J. Mar. Syst., 94, 52–63,
- 737 doi:10.1016/j.jmarsys.2011.10.008, 2012a.

- 738 Vázquez-Rodríguez, M., Pérez, F.F., Velo, A., Ríos, A.F., and Mercier, H.: Observed acidification trends in
- 739 North Atlantic water masses, Biogeosciences, 9, 5217–5230, doi:10.5194/bg-9-5217-2012, 2012b.
- 740 Velo, A., Pérez, F.F., Tanhua, T., Gilcoto, M., Ríos, A.F., and Key, R.M.: Total alkalinity estimation using MLR
- 741 and neural network techniques, J. Mar. Syst., 111–112, 11–18, doi:10.1016/j.jmarsys.2012.09.002, 2013.
- 742 Wakita, M., Watanabe, S., Honda, M., Nagano, A., Kimoto, K., Matsumoto, K., Kitamura, M., Sasaki, K.,
- 743 Kawakami, H., Fujiki, T., Sasaoka, K., Nakano, Y., and Murata, A.: Ocean acidification from 1997 to 2011 in
- the subarctic western North Pacific Ocean, Biogeosciences, 10, 7817-7827, doi:10.5194/bg-10-7817-2013,
- 745 2013.
- Wallace, W.R.: Storage and transport of excess CO₂ in the oceans: The JGOFS/WOCE global CO₂ survey, in:
 Ocean Circulation and Climate [Siedler, G., Church, J., and Gould J. (eds.)], Academic Press, 489–521, 2001.
- Waugh, D.W., Hall, T.M., McNeil, B.I., Key, R. and Matear, R.J.: Anthropogenic CO₂ in the oceans estimated
 using transit time distributions, Tellus B, 58, 376–389, doi:10.1111/j.1600-0889.2006.00222.x, 2006.
- Yashayaev, I.: Hydrographic changes in the Labrador Sea, 1960-2005, Prog. Oceanogr., 73, 242–276,
 doi:10.1016/j.pocean.2007.04.015, 2007.
- 752 | Yashayaev, I., and Dickson, R.R.: Transformation and fate of overflows in the Northern North Atlantic. In:
- Dickson, R.R., Jens, M., Rhines, P. (Eds.), Arctic-Subarctic Ocean Fluxes: Defining the Role of the Northern
 Seas in Climate. Springer, Science + Business Media B.V., P.O. Box 17, AA Dordrecht, The Netherlands, pp.
 505–526, 2008.
- Yashayaev, I., Bersch, M., and van Aken, H.M.: Spreading of the Labrador Sea Water to the Irminger and
 Iceland basins, Geophys. Res. Lett., 34, L10602, doi:10.1029/2006GL028999, 2007.
- 758 Yashayaev, I., Holliday, N.P., Bersch, M., and van Aken, H.M.: The History of the Labrador Sea Water:
- 759 Production, Spreading, Transformation and Loss, in: Arctic–Subarctic Ocean Fluxes: Defining the Role of the
- 760 Northern Seas in Climate [Dickson, R.R., Meincke, J., and Rhines, P. (eds.)], Springer Netherlands, 569–612,
- 761 2008.
- 762 Zunino, P., Pérez, F.F., Fajar, N.M., Guallart, E.F., Ríos, A.F., Pelegrí, J.L., and Hernández-Guerra, A.:
- 763 Transports and budgets of anthropogenic CO_2 in the tropical North Atlantic in 1992–1993 and 2010–2011, Glob.
- 764 Biogeochem. Cycles, 29, 2014GB005075, doi:10.1002/2014GB005075, 2015.

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Table 1: List of hydrographic cruises used in this study (Fig. 1a). P.I. denotes principal investigator, and #St the number of stations selected used here, and measurements refers to the seawater CO₂ system measurements performed during these cruises.

Cruise Name	Expocode	Month/Year	Vessel	P.I.	#St	Measurements	Reference
TTO-NAS L6	316N19810821	08-09/1981	Knorr	W.J. Jenkins	11	$A_{\rm T}$ and DIC	Takahashi and Brewer (1986)
AR07E	64TR91_1	04-05/1991	Tyro	H.M. van Aken	12	DIC	Stoll et al. (1996)
A01E	06MT18_1	09/1991	Meteor	J. Meincke	15	A _T and DIC	Meincke and Becker (1993)
A01E	06MT30_3	11-12/1994	Meteor	J. Meincke	27	DIC	Koltermann et al. (1996)
AR07E	06MT39_5	08–09/1997	Meteor	A. Sy	32	DIC	Rhein et al. (2002)
OVIDE 2002	35TH20020610	06-07/2002	Thalassa	H. Mercier	38	pH and A_T	Lherminier et al. (2007)
OVIDE 2004	35TH20040604	06-07/2004	Thalassa	T. Huck	56	pH and A_T	Lherminier et al. (2010)
OVIDE 2006	06MM20060523	05-06/2006	Maria S. Merian	P. Lherminier	44	pH and A_T	Gourcuff et al. (2011)
OVIDE 2008	35TH20080610	06-07/2008	Thalassa	H. Mercier	45	pH and A_T	Mercier et al. (2015)
OVIDE 2010	35TH20100610	06/2010	Thalassa	T. Huck; H. Mercier	46	pH and $A_{\rm T}$	Mercier et al. (2015)
CATARINA ^a	29AH20120623	06-07/2012	Sarmiento de Gamboa	A.F. Ríos	44	pH and $A_{\rm T}$	This work
GEOVIDE ^a	35PQ20140517	05-06/2014	Pourquoi Pas?	G. Sarthou	31	pH and A_T	This work
58GS20150410	58GS20150410	04-05/2015	G.O. Sars	A. Olsen	10	A _T and DIC	Fröb et al. (2016)

768 769 ^aBoth CATARINA (<u>http://catarina.iim.csic.es/en</u>) and GEOVIDE (<u>http://www.geovide.obs-vlfr.fr</u>) cruises contain the OVIDE section (<u>http://wwz.ifremer.fr/lpo/La-recherche/Projets-en-cours/OVIDE</u>), and in the study are referred <u>to</u> as OVIDE 2012 and 2014, respectively.

Table 2: Mean values \pm confidence interval of pressure (in dbar), potential temperature (θ , in °C), salinity, Apparent Oxygen Utilization (AOU, in μ mol·kg⁻¹), total alkalinity (A_T, in μ mol·kg⁻¹), anthropogenic CO₂ (C_{ant}, in μ mol·kg⁻¹) and pH at total scale and $\frac{25^{\circ}\text{Cin situ conditions of temperature and pressure}{\text{Plans Starsenergy}}$ (pH_{Tis25}) for the bottom waters of the Iberian Abyssal Plain sampled during the seven OVIDE cruises. "#<u>N</u>" represents the number of data considered in each cruise and "±" the standard deviation. The last row represents the inter-cruise confidence interval (i.e., the confidence intervalstandard deviation of the mean values across the seven eruises).

Year (<mark>nN</mark>)	Pressure	θ	Salinity	AOU	A _T	Cant	рН _{т25<u>іs</u>}
2002 (144)	4205 <u>± 1052</u>	2.182 ± 0. <u>160080</u>	34.913 ± 0.01608	86.1 ± 4 <u>2</u> .0	2351 ± <mark>63</mark>	6.4 ± 2.6<u>1.3</u>	7.740 <u>8. 013</u> ± 0.00 <u>63</u>
2004 (158)	4263- <u>± 998</u>	2.162 ± 0. <u>150075</u>	$34.908 \pm 0.014 \underline{07}$	87.1 ± 2.8<u>1.4</u>	$2352\pm \underline{63}$	6.2 ± <u>1.</u> 2 . 4	7.741 <u>8.013</u> ± 0.00 <u>63</u>
2006 (132)	4252 ±1058	2.170 ± 0. <u>164082</u>	$34.913 \pm 0.0 \underline{1608}$	85.4 ± <u>3.2</u> <u>1.6</u>	$2350\pm \underline{\textbf{63}}$	6.2 ± 2.6<u>1.3</u>	7.741 <u>8.014</u> ± 0.006 <u>3</u>
2008 (125)	4206 <u>± 1022</u>	2.179 ± 0. 150<u>075</u>	34.911 ± 0.01407	84.9 ± 3.6<u>1.8</u>	$2353\pm \underline{84}$	$7.0 \pm \frac{3.2}{1.6}$	7.744 <u>8.016</u> ± 0.00 <u>63</u>
2010 (131)	4312 ±1048	2.163 ± 0. <u>154077</u>	$34.908 \pm 0.0 \underline{1608}$	85.9 ± 3.2<u>1.6</u>	2351 ± <u>63</u>	7.0 ± <u>1.</u> 2 . 4	7.740 <u>8.013</u> ± 0.004 <u>2</u>
2012 (102)	4397 ±1052	2.149 ± 0. <u>154077</u>	$34.909 \pm 0.0 \frac{1608}{1000}$	87.9 ± 3.2<u>1.6</u>	2352 ± <u>63</u>	5.1 ± <u>1.</u> 2 .4	7.742 <u>8.015</u> ± 0.004 <u>2</u>
2014 (54)	4441 ± 954	2.141 ± 0. 138<u>069</u>	$34.904 \pm 0.0\underline{1407}$	87.4 ± 2.6<u>1.36</u>	2353 ± <u>63</u>	5.5 ± 3.0<u>1.5</u>	7.743 <u>8.016</u> ± 0.00 <u>63</u>
	70	0. 011<u>015</u>	0.00 <mark>2<u>3</u></mark>	0.8 <u>1.1</u>	0.8 <u>1.1</u>	0. <u>57</u>	0.001 <u>5</u>

777Table 3: Observed temporal changes of pH at total scale and in situ conditions (in situ temperature and pressure;778 $\frac{dpH_{TIS}}{dt} obs \left(\frac{dpH_{TIS}}{dt}\right)_{obs}$) for the main water masses in the Irminger and Iceland basins for the period 19891–2015. pH779changes caused by the main drivers (in situ temperature, T_{is} ; salinity, S; total alkalinity, A_T ; total dissolved inorganic780carbon, DIC; the latter decomposed into its anthropogenic CO_{25} , C_{ant} ; and natural DIC, components, C_{ant} , and C_{nats} 781respectively) are also shown, as well as the pH changes result of determined as the sum of the pH changes caused by782the individual drivers ($\frac{dpH_{TIS}}{dt}$ model ($\frac{dpH_{TIS}}{dt}$). All the trends are calculated based on the annually interpolated783values and are in 10⁻³ pH units·yr⁻¹. Values in parenthesis are the percentages of the observed pH change explained by784each one of its drivers. Confront Fig. 1 for water mass acronyms.

		$\left(\frac{dpH_{Tis}}{dt}\right)_{obs}$	$\frac{c\partial pH_{Tis}}{\partial T_{is}} \frac{dT_{is}}{dt}$	<u>ðpH_{Tis} dS</u> ðS dt	$\frac{\partial p H_{TIS}}{\partial A_T} \frac{dA_T}{dt}$	ðpH _{Tis} dDIC ðDIC dt	<u>ðpH_{Tis} dC_{ant} ðDIC dt</u>	<u>ðpH_{Tis} dC_{nat} ðDIC dt</u>	$\left(\frac{dpH_{TIS}}{dt}\right)_{total}\frac{dpH_{TH}}{dt}$
	SPMW	-1. 3184 ± 0.08	-0.2404 ± 0.068 (182)	$-0.02\underline{1} \pm 0.04\underline{08}$ (<u>21</u>)	0.296 ± 0.057 (- 2214)	$\frac{-1.342.05}{(102\underline{11})} \pm 0.12\underline{1}$	$\frac{-1.592.21}{(1240)} \pm 0.104$	0. <u>2416</u> ± 0.0610 (- 49)	-1.3285 ± 0.145 (100.45)
	nLSW	-1. <u>3060</u> ± 0. <u>0810</u>	-0.223 ± 0.023 (1714)	$-0.01\frac{1}{20} \pm 0.00\frac{1}{2}$ (1)	0.25 ± 0.0 <u>13</u> (- 19 <u>6</u>)	-1. 3161 ± 0.08 (101)	-1.0983 ± 0.136 (84114)	-0.22 ± 0.134 (17- 14)	$-1.\overline{3061} \pm 0.089$ (100. <u>26</u>)
Irminger	cLSW	-1. 0659 ± 0.08 <u>6</u>	-0.440 ± 0.043 (1325)	$-0.0\frac{40}{4} \pm 0.43$ (23)	0.3170 ± 0.065 (-	-1.2285 ± 0.407 (1156)	-0.545 ± 0.047 (5134)	- <u>1.310.68</u> ± 0. <u>1109</u> (64 82)	-1.0760 ± 0.1209 (100.43)
	ISOW	- <u>1.310.82</u> ± 0.08 <u>5</u>	-0.0 39 ± 0.02 (- 3 7	$-0.00_{40} \pm 0_{-2.3} (01)$	-0. <u>0129</u> ± 0. <u>56</u> (-1 22)	$\frac{1.50.85}{(103 15)} \pm 0.407$	-0.7499 ± 0.067 (8976)	-0.4150 ± 0.079 (1439)	$\frac{-1.310.83}{(100.4\underline{1})} \pm 0.11\underline{09}$
	DSOW	- <u>1.470.91</u> ± 0.09 <u>5</u>	-0.016 ± 0.035 (6 <u>11</u>)	$-0.00 + 15 \pm 0.23$ (1)	0.2355 ± 0.067 (-	-1.0985 ± 0.1208 (114926)	$-\frac{1.270.89}{(9\underline{87})} \pm 0.089$	$-0.\frac{2058}{2239} \pm 0.079$	- <u>1.480.92</u> ± 0.14 <u>2</u> (100.7 <u>6</u>)
	SPMW	-1. <u>1859</u> ± 0.09 <u>15</u>	-0.4016 ± 0.0813 (3410)	-0.0316 ± 0.011 (21)	$0.44\underline{17} \pm 0.07\underline{12} (-37\underline{11})$	-1.260 ± 0.147 (102 <u>1</u>)	$(-1,2554 \pm 0.0713)$ (10697)	-0.0 <mark>56</mark> ± 0.0 68 (-4)	-1. <u>+960</u> ± 0. 1524 (100. 69)
	nLSW	- <u>1.090.80</u> ± 0.0 <u>≤7</u>	0.0 <u>32</u> ± 0.0 <u>+2</u> (- 4 <u>2</u>)	$0.00_{43} \pm 0.00_{42}$ (- $\frac{10}{10}$)	-0.0610 ± 0.047 (- 79)	$-\frac{1.030.90}{(11295)} \pm 0.046$	$\frac{-1.680.97}{(12154)} \pm 0.125$	0.0765 ± 0.0911 (- 960)	$\frac{-1.100.81}{(10\underline{10}.04)} \pm 0.06\underline{10}$
Iceland	cLSW	-0. <u>976</u> ± 0. 06<u>11</u>	-0.0 56 ± 0.02 (-6)	-0.007 ± 0.002 (-1)	0.1 <u>98</u> ± 0.0 5 9 (- 24 <u>18</u>)	-1.049 ± 0.0714 (13212)	-0.6998 ± 0.058	-0.3112 ± 0.0611 (4112)	-0.7798 ± 0.0917 (1001.40)
	ISOW	-0. 6190 ± 0.06 <u>9</u>	-0.03 ± 0.01 (-4)	$-0.00_{43} \pm 0.001$ (- $\frac{10}{10}$)	0.3111 ± 0.107 (- 512)	-0.959 ± 0.0814 (15610)	-0.5495 ± 0.078 (89105)	-0.4104 ± 0.0811 (67 <u>5</u>)	-0.6191 ± 0.108 (1001.16)

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787 Figure 1: (a) Sampling locations of the thirteentwelve cruises used in this study (19891–2015) plotted on bathymetry 788 (500 m intervals). The black line shows the boundary between the Irminger and the Iceland basins constituted by the 789 Reykjanes Ridge. CGFZ = Charlie–Gibbs Fracture Zone. (b) Limits of the layers and basins considered in this study 790 791 plotted on top of the mean-salinity of distribution for the sections 2004 cruise. The isopycnals delineating the layers are defined by potential density ($\sigma_{0,7}$ referenced to 0 dbar, σ_0 ; 1000 dbar, σ_1 ; and 2000 dbar, σ_2 ; all in kg·m⁻³), and the 792 vertical white line is the limit (Reykjanes Ridge) between the Irminger (left) and Iceland basins (right). The dashed 793 vertical lines represent the Longitude axis marks. The layer acronyms are Subpolar Mode Water (SPMW), upper and 794 classical Labrador Sea Water (uLSW and cLSW, respectively), Iceland-Scotland Overflow Water (ISOW) and 795 Denmark Strait Overflow Water (DSOW).



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Figure 2: <u>Mean-Dd</u>istributions along the cruise track, from Greenland (left) to the Iceland basin (right) over study period (19891–2015), for: (a) potential temperature (θ , in °C), (b) salinity, (c) pH at total scale and in situ conditions (pHTis), (d) total alkalinity (AT, in µmol·kg⁻¹), (e) apparent oxygen utilization (AOU, in µmol·kg⁻¹), (f) total dissolved inorganic carbon (DIC; in µmol·kg⁻¹), (g) natural DIC (Cnat, in µmol·kg⁻¹) and (h) anthropogenic CO₂ (Cant, in µmol·kg⁻¹) for the 2004 cruise. The dashed vertical lines represent the Longitude axis marks.

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Figure 3: Temporal evolution of average pH at total scale and in situ conditions (pH_{Tis}) in the main water masses of the Irminger (a) and Iceland (b) basins, between 19891 and 2015. Each point represents the average pH_{Tis} of a 804 805 particular layer (SPMW (red dots), uLSW (blue dotsdiamonds), cLSW (black dotsasterisks), ISOW (green dotssquares) and DSOW (magenta dotsstars)) at the time of each cruise (Table S1). The error bars are two times the error of the mean $(2\sigma = 2x(\text{Standard Deviation})/\sqrt{N})$, where N is the number of samples of each layer). The inset boxes legends also give the trends (in 10^{-3} pH units yr⁻¹) ± standard error of the estimate and the correlation coefficients (r²), resulting from the annually interpolated values. *** denotes that the trend is statistically significant at the 99% level (p-value < 0.01). Confront Fig. 1 for layer acronyms.

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Figure 4: Temporal evolution between 19891 and 2015 of average (a and b) in situ temperature (T_{is} , in °C) and (c and d) salinity in the main water masses of the Irminger (a and c) and Iceland (b and ed) basins. Each point represents the average property of a particular layer (SPMW (red dots), uLSW (blue dotsdiamonds), cLSW (black dotsasterisks), ISOW (green dotssquares) and DSOW (magenta dotsstars)) at the time of each cruise (Table S1). The error bars are 2σ . The inset boxes[egends also give the trends (in 10^{-3} units·yr⁻¹) ± standard error of the estimate and the correlation coefficients (r²), resulting from the annually interpolated values. *** denotes that the trend is statistically significant at the 90% level (p-value < 0.1), ** at the 95% level (p-value < 0.05), and *** at 99% level (p-value < 0.01). Confront Fig. 1 for layer acronyms.

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Figure 5: Temporal evolution between 19891 and 2015 of average (a and b) total alkalinity (A_T , in µmol·kg⁻¹) and (c and d) total dissolved inorganic carbon (DIC, in µmol·kg⁻¹) in the main water masses of the Irminger (a and c) and Iceland (b and d) basins. Each point represents the average property of a particular layer (SPMW (red dots), uLSW (blue dotsdiamonds), cLSW (black dotsasterisks), ISOW (green dotssquares) and DSOW (magenta dotsstars)) at the time of each cruise (Table S1). The error bars are 2σ . The inset boxes[egends also give the trends (in µmol·kg⁻¹·yr⁻¹) ± standard error of the estimate and the correlation coefficients (r²), resulting from the annually interpolated values. **** denotes that the trend is statistically significant at 90% level (p-value < 0.1), and *** at the 99% level (p-value < 0.01). Confront Fig. 1 for layer acronyms.

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830 Figure 6: Temporal evolution between 19891 and 2015 of average (a and b) anthropogenic CO₂ (C_{ant}, in µmol·kg⁻¹) 831 and (c and d) natural DIC ($C_{nat} = DIC - C_{ant}$, in µmol·kg⁻¹) values in the main water masses of the Irminger (a and c) 832 and Iceland (b and ed) basins. Each point represents the average property of a particular layer (SPMW (red dots), 833 uLSW (blue dotsdiamonds), cLSW (black dotsasterisks), ISOW (green dotssquares) and DSOW (magenta dotsstars)) 834 at the time of each cruise (Table S1). The error bars are 2σ . The inset boxes legends also give the trends (in μ mol·kg 835 1 ·yr⁻¹) ± standard error of the estimate and the correlation coefficients (r²), resulting from the annually interpolated 836 values. ******** denotes that the trend is statistically significant at the 90% level (p-value < 0.1), and *** at the 99% level 837 (p-value < 0.01). Confront Fig. 1 for layer acronyms.