

REVIEWER #3

M. Vázquez-Rodríguez, F. F. Pérez, A. Velo, A. F. Ríos, and H. Mercier (2012), Observed trends of anthropogenic acidification in North Atlantic water masses. Biogeosciences Discuss. (bg-2012-83) 9:3003-3030

ANSWERS TO COMMENTS AND QUESTIONS ARE IN BLUE FONT. FULL DETAILS OF ALL REFERENCES CITED IN THE ANSWERS ARE PROVIDED IN THE REFERENCE LIST, AT THE END OF THIS LETTER / REVISED VERSION OF THE MANUSCRIPT.

Dear reviewer,

Thanks a lot for your input. Your comments and suggestions have greatly helped improving this version of the manuscript (attached at the end of this document), which has changed substantially with respect to the previous one. The main modifications include the following:

- 1) Methods section: Section 2.2 where the averaging and basin normalization of data is described is more concise now and makes clear that such data treatment does not aim at separating the anthropogenic and the natural acidification signals (this was not explained well enough in the previous version of the manuscript), but rather calculate small pH corrections to the measurements ($\Delta\text{pH}_{\text{SWS25-BA}}$) to avoid potential sampling biases by centering / normalising the data from single cruises to the average basin conditions.
- 2) Figure 2 has been updated and now all panels include the isopycnals that separate the studied water masses in each basin, as listed in Table 2 and described in section 2.2 and Fig. 1b.
- 3) We updated the uncertainty of pH measurements in Table 1. Table 2 (included as Supplementary information in the previous manuscript version) now includes the pH averages per water mass and basin obtained from a) direct measurements (pH_{SWS25}); b) basin-and-layer normalization (correction) element ($\Delta\text{pH}_{\text{SWS25-BA}}$); and c) basin-normalized pH averages ($\text{pH}_{\text{SWS25-BA}}$), after the expression in equation 1 ($\text{pH}_{\text{SWS25-BA}} = \text{pH}_{\text{SWS25}} + \Delta\text{pH}_{\text{SWS25-BA}}$). This way it is made explicitly clear what the orders of magnitude of the normalization of data are in each case, and how the measured and normalized pH data compare to each other.
- 4) Discussion section: Comparison of results with data from time series stations ESTOC and BATS; Calculation of expected rates of acidification due to C_{ant} entry (i.e., anthropogenic acidification) from the C_{ant} storage rates in Pérez et al. (2010) and comparison of those acidification rates with the ones here obtained (Fig. 3) from direct measurements.

After all these major modifications motivated by your comments, the reply to most of the suggestions made in your original review letter are answered by making reference to the revised manuscript version, rather than point-by-point. This is the reason why we have included it at the end of this letter.

We hope you find the changes we made in this new version respond satisfactorily to your detailed review and critic of the original document.

With our best regards.

Marcos Vázquez-Rodríguez and co-authors

General Comments

The authors have assembled a vast dataset of carbonate system constraints measured over the last three decades. They have verified that the first set of quality control checks have been performed upon this data and have taken some efforts to see that the assembled data are intercomparable. They have then used this dataset to determine the evolution of relationships between various parameters and the measured or calculated pH. Finally, they have applied the determined relationships to an annually averaged property distribution to estimate the temporal evolution of the pH distribution from the temporal evolution of the regression of pH against other properties. The authors' main contribution in this paper is a set of rates of acidification for a number of isopycnal layers in the North Atlantic.

This paper is making a comment on the acidification of deeper and intermediate waters that is important and likely correct, and it does so concisely. However, the paper has several large flaws in its current state: the description of the dataset quality control efforts is incomplete, the description of and the justification for the analysis used is lacking, [As mentioned in point 1\) on the general comments above, section 2.2 and, in particular, sub-section 2.2.1 have been modified substantially to improve this common critic from all of the reviewers.](#) and the conclusions are essentially a restatement of other work published by the same researchers given the assumptions implicit in the methods used. [We have modified the Conclusions section accordingly with the new structure and content in the revised manuscript. It is as follows:](#) *“The progressive acidification of North Atlantic waters has been assessed from direct observations of pH spanning the last three decades. The increasing atmospheric CO₂ concentrations have largely affected the pH of surface and intermediate waters in the three studied North Atlantic regions, at varying extents. Most importantly, the LSW has shown very high acidification rates that are amongst the highest in the NASPG. In the Irminger basin, the acidification rate of cLSW responds to that expected from the influence of C_{ant}, while in the Iceland basin only about 50% of the observed pH change in the cLSW is anthropogenic. The SAIW has the fastest acidification rate observed (-0.0019±0.0002 yr⁻¹), and 75% of this pH decrease is anthropogenic. In contrast, the C_{ant} contribution to the acidification rates in the ENACW is partially compensated by the ventilation of this water mass thus explaining the moderate acidification rates observed in the upper layers of the ENA basin (compared to the Iceland and Irminger basins). Predictions from an observation-based extrapolation of the current acidification trends and rates are in agreement with model results (Caldeira and Wickett, 2005; Orr et al., 2005) in surface layers. However, our results indicate that the intermediate waters of the North Atlantic (LSW in particular) are getting acidified more rapidly than what some models predicted.”* Given that the same dataset is used for the earlier published paper, this paper can also not be viewed as a confirmation of the earlier findings. That is definitely not our intention. The work from Pérez et al. 2010 stands alone by itself and does not need any further confirmation or contribution based on our analysis. Even though our study shares the dataset in the work from Pérez et al. 2010 (with the exception of the OVIDE 2008 data, which Pérez et al. did not use), there is a fundamental difference as you pointed earlier, which is that we look at a totally different variable and issue: pH (which is a direct measurement) and not anthropogenic CO₂ (that needs to be estimated from the measurements). There are processes that affect pH and not C_{ant} and vice versa, that is why our study is relevant and legitimate. Also, one of the main findings we try to highlight with our work is how fast the acidification rates of intermediate and deep waters in the NASPG are (Iceland and Irminger basin in particular), and none of that is mentioned in Pérez et al. 2010, or within their goals. In this revised version we have used the fact that Pérez et al. 2010 refer to the same water masses we do, and they use almost the same dataset, to improve our discussion section. We have calculated the expected pH change due to the entry of C_{ant} in each layer, using the C_{ant} storage rates in Pérez et al. 2010, and compared the results with the acidification rates we obtained. If at all, this should be seen as an advantage that improves significantly the discussion in our manuscript, and it adds to the results here provided.

Scientific Comments

Many of my concerns have already been brought up by Anonymous Reviewer #1, with whom I broadly agree. We invite you to read the answers posted to Reviewer's #1 comments. Some of them are common to yours. One exception is that I am not worried by potential errors created by the use of the SWS scale for pH. It is important that a single scale be used throughout, as the authors have done, and there should be essentially no uncertainties in any trends found that originate from the choice of scale. The author's comment that a single scale must be used to avoid errors from the choice of scale (on the order of 0.01 pH units) is correct, but could perhaps be more clearly phrased. The second phase of the data quality control (2QC) of the CARINA database (which we have used in our work) has standardized the process of pH data scale unification and cruise adjustments. The details are given in the work from Velo et al. 2010 (<http://www.earth-syst-sci-data.net/2/133/2010/essd-2-133-2010.html>). Additionally, more information on the uncertainties is now provided on Tables 1 and 2. We have rewritten this part of the paragraph to accommodate this suggestion from you and the other reviewers. We hope it is clearer now: "*...All pH measurements that had not been originally reported in the seawater scale (pH_{SWS} ; Millero, 2007) were converted to it from either the total or the NBS pH scale using the corresponding acid dissociation constants (Dickson and Millero, 1987), following the CARINA database second quality control recommendations for pH data scale unification and cruise adjustments (Velo et al., 2010). The acid dissociation constants for HF or HSO_4^- (Millero, 2007) were used to convert pH values originally reported in the total scale (those measured spectrophotometrically; Table 1) to the SWS scale. The pHs measured potentiometrically were all reported on the NBS scale and were converted to the SWS scale as specified in Pérez and Fraga (1987). Some of the cruises listed in Table 1 did not perform direct pH measurements but obtained total alkalinity (A_T) and dissolved inorganic carbon (C_T) data. In such cases the pH values were calculated in the SWS scale from A_T and C_T data using the thermodynamic equations of the carbon system (Dickson et al., 2007) and a set of CO_2 dissociation constants (Dickson and Millero, 1987). The pH estimated accuracy ranges from ± 0.002 to ± 0.008 depending of the used methodology at each cruise (Table 1).*"

The problems with this manuscript largely come from the choice of pH as a variable with which to assess long term trends. This variable is problematic for trend analysis for two reasons:

1. First (and I disagree with the authors on this point) pH measurements have large *accuracy* uncertainties (though excellent *precision* when using Clayton and Byrne's [1993] spectrophotometric analytical methods).

Yao et al. [2007] have demonstrated that impurities in meta-cresol dyes typically used for spectrophotometric analyses can lead to significant differences in pH values measured for a single sample of seawater when dye from different manufacturers is used. This work has been expanded upon by the Byrne lab [Liu et al., 2011], who show that the pH measured by individual batches of dye can be in disagreement with one another by as much as ± 0.01 pH units. It is possible that steps have been taken to adjust measured pH data for this - or that only a single batch of dye has been used for all measurements - but this large potential source for error needs to be addressed. Concerning the pH measurements in which our lab and team have been involved (FOUREX and all of the OVIDE cruises): We use the *m*-cresol indicator dye supplied by Sigma-Aldrich, and the batch has been checked for impurities in our lab using HPLC techniques (as in Liu et al. 2011). None of the impurities described in Liu et al. 2011 have been detected in our indicator batch. On the other hand, Yao et al. 2007 reports that that the *m*-cresol from Sigma-Aldrich produces biases between 0.001 and 0.004, which is within the pH ranges in this paper, compared to the *m*-cresol from Kodak used in Clayton and Byrne, 1993. Additionally, the internal consistency analysis of the FOUREX and all of the OVIDE cruises, included in the CARINA database, did not produce biases larger than ± 0.005 (Velo et al., 2010;

<http://www.earth-syst-sci-data.net/2/133/2010/essd-2-133-2010.html>).

The lack of an appropriate reference material is an additional concern for detection of trends in pH. Tris buffers, rarely used at sea, have been shown to have uncertainties on the order of ± 0.005 in pH [Clayton and Byrne, 1993; DelValls and Dickson, 1998; Buck et al. 2002; Nemzer and Dickson, 2005; Marion et al. 2011]. Certified seawater reference materials (CRMs) have not been available for the entire sampling period considered in this paper, so the author's claim that they have been used to check these measurements is confusing. Furthermore, CRMs are not certified for pH measurements, and therefore the use of these seawater samples for pH calibration must rely upon a calculation of pH from carbonate constants and the certified values of alkalinity, C_T , and nutrient concentrations. The uncertainties on pH values estimated from carbonate constant sets are considerable. Certainly CRMs are not certified as references for pH measurements. However, there are other quality control (QC) methods that are used in the absence of such an analytical reference, like those used to compile the CARINA database (Velo et al., 2010), where they applied a cross-over analysis technique to check the results of C_T , A_T and pH (both measured and calculated) in more than 100 cruises. If the biases mentioned in Liu et al. 2011 had appeared in any of the data from those cruises, then the cruises in the CARINA database that had reported C_T calculated from pH and A_T measurements would have proved to be inconsistent (higher C_T values) with the values from the cross-over cruises that reported measured C_T coulometrically... and that has not been the case. As mentioned above, we participated on the OVIDE and FOUREX cruises measuring spectrophotometric pH and potentiometric A_T , and reported C_T calculated from those pH and A_T measurements. The CARINA cross-over analysis showed that those cruises had reported consistent C_T values with the corresponding cross-over cruises that had measured C_T directly using coulometric techniques (<http://www.earth-syst-sci-data.net/2/177/2010/essd-2-177-2010.html>). Hence, given the foregoing evidence, the recent results and suggestions in Liu et al. 2011 must still be taken under caveat until they are further verified in future studies. The data here used, our lab HPLC analysis, spectrophotometric pH measurements and the cross-over intercomparison with other cruises in the NASPG do not show biases in our data, as suggested by the results in Liu et al. 2011. Consider that 6 commonly-used sets of carbonate constants will yield pH values that range by as much as 0.03 in pH for seawater of standard composition [Hansson 1973; Mehrbach et al. 1973; Dickson and Millero 1987; Goyet and Poisson 1989; Roy et al. 1994; Millero et al. 2006]. This suggests that the author's unsubstantiated estimate of ± 0.0034 uncertainty is too small for these values. The constants from Hansson 1973; Goyet and Poisson 1989; and Roy et al. 1994, are recommended for use in synthetic seawater measurements, and they are not valid when applied to natural seawater (Millero et al., 2007). The constants from Dickson and Millero 1987; Lueker et al. 2000; and Millero et al. 2007 all give very similar results, within the cited error band. The choice of the constants used in our study was partly motivated because they are the same ones used during the second quality control (2QC) of the CARINA dataset (our source of data), for the sake of consistency and reliability. Indeed, their uncertainty estimate is smaller even than the pH uncertainty that would be expected ($\sim \pm 0.008$ pH units) if their reported typical analytical accuracy uncertainty for total alkalinity ($\pm 4 \mu\text{mol kg}^{-1}$) were the *only* uncertainty on pH, and there were no uncertainty in the carbonate constants themselves. In this regard, using the water mass approach that we did allows analysing groups of samples that have very homogeneous properties, which has the following advantages for our purposes: 1) It allows to check for biases in the measurements, since we have a large number of replicates; and 2) The potential non-linearities that could exist on the pH values (measured or calculated ones) would not affect significantly the obtained trends since, within each water mass, we are dealing with a very small variability range. Finally, even if one were to trust a CRM pH value, this would allow for only a single point calibration at the approximate pH of the surface of the North Pacific gyre, and the Clayton and Byrne [1993] method has been shown to have a pH dependence to its disagreement with pH values estimated from carbonate system equations [McElligott et al., 1998]. If that were the case then it would represent a minor issue, considering that in the NASPG the pH variability range is about three times smaller than in the North Pacific.

This trend analysis needs to demonstrate that non-systematic accuracy uncertainties are not biasing the results. The switch in methods of pH estimation from mostly calculated to mostly spectrophotometrically measured (table 1) suggests that systematic errors for these two approaches could also bias the early record relative to the late record, and could therefore lead to errors in trend estimates. The differences in methods could result in the drops in pH seen between the first two pH maps in Figure 2 (where the first is calculated and the second is determined spectrophotometrically), just as changes in the manufacturer of dye used could result in the changes seen between the second map and each subsequent map (provided this was not adjusted for). Please, refer to the above comments on this issue. In summary, there are no biases on the calculated trends, or funded reasons to think otherwise, mainly because: 1) All of the data here used have passed the 2QC of the CARINA dataset; and 2) The noise and “biases” in the *NADW*, which is the most isolated water mass in this study (with no statistically significant signs of pH variation over the study period), consistently show an average pH of 7.727 ± 0.004 , for all 13 cruises used in our study, from 1981 to 2008. This is a solid proof that supports the high quality of our data and the robustness of the acidification trends obtained.

2. Secondly, pH trends are not well-represented by multiple linear regression analysis (MLR): pH does not mix linearly, nor does it respond linearly to changes in total dissolved inorganic carbon (C_T). Therefore - even assuming Redfield ratios of remineralization are appropriate - pH would not be expected to co-vary linearly with apparent oxygen utilization (AOU) or with physical mixing variables such as potential temperature or salinity. MLR is only appropriate when attempting to account for processes that change the properties considered in a linear way (see discussion by Li and Peng [2002] for more on how MLR implicitly represents linear mixing and remineralization). To see how non-linearities could be problematic for this analysis, consider seawater in a small container in which organic matter of a constant elemental ratio is being uniformly remineralized at a constant rate. A MLR analysis relating the various properties of this seawater at different points in time would obtain a consistent relationship between AOU and C_T , but the relationship between AOU and pH would be constantly changing as the pCO_2 increases and the Revelle factor changes. This could lead to differences in MLR coefficients simply from the sampling pattern of each cruise. When you also allow for non-linear changes in pH from essentially linear mixing of potential temperature, alkalinity, and C_T , the MLR outputs become very difficult to correctly interpret. This is right, but this problem is tackled by working within the chosen isopycnals that delimit well-established water masses in the NASPG, with highly homogeneous properties, as mentioned in one of the above answers. Also, Table 2 (an updated version of former supplementary tables) clearly shows that the variability ranges are quite low and thus it is feasible to apply an MLR technique here, within each layer, and still avoid non-linearity issues that you mention. Those non-linearities are typical in surface-to-bottom water column analysis where the variability of AOU is of the order of 10 times larger than the one recorded within any of the layers (water masses) here considered, as shown in new Table 2.

Another problem with MLR analysis is the need to show that long term trends in water mass temperature and salinity do not also play a role. Long term warming or freshening of water masses will “move” isopycnals to deeper depths where, typically, there is more C_T and pH is lower [Wong et al., 2001; Aoki et al., 2005]. Therefore all trends demonstrated here could be instead interpreted as long term temperature and salinity trends biasing MLR results. While this seems unlikely to be the dominant source for long term pH changes in these water masses, this source of uncertainty should be addressed. This is true. However, in the particular case of the NASPG, where convection is so strong, the thickness of each layer is of the order of 100 times larger than the variability of the isopycnals’ depth (on the order of 10 meters), and this would not affect significantly the average properties of the selected water masses, nor the calculated trends.

Collectively these problems with trend detection in pH raise the question “why examine trends

in pH instead of C_T ?" Ignoring for the moment that C_T has been done for this region, doing pH separately can be motivated by the importance of pH and carbonate ion availability for ecosystem dynamics. Yes, amongst other interests. However, the specific connection between deepwater acidification and the health of deep-water benthic and pelagic organisms (deep specifically) is not made until the discussion section. Evaluating or quantifying the aftermaths of acidification on living organisms is not within the scope of our study. The former manuscript version mentioned at the very end some of the possible effects briefly and in an unsubstantiated way, and we decided to remove this part of the discussion. However, we believe that our results will be of help and interest for future studies aiming to investigate the effects of ocean acidification on deep-water coral reef or pelagic ecosystems. When one considers that the anthropogenic C_T trend has been estimated [Pérez et al., 2010], it becomes less clear why anthropogenic pH trends need also be assessed. Just because of the fact that pH and C_{ant} content do not necessarily correspond each other exactly. This, and the fact that we had the possibility to make such a study from direct measurements are some of the main reasons that make the acidification of the NASPG an interesting topic on its own, never covered before in the way we have (observation-based, over three decades, and in the entire water column). This is easily corroborated from the results presented in our study, none of which are mentioned or covered in Pérez et al. 2010. While C_T and pH do contain independent information, the determination of trends in pH from trends in C_T may be done provided one assumes that there are no long term trends occurring in total alkalinity, salinity, nutrients, or temperature. All of these assumptions are explicitly or implicitly made by this paper (implied by the choice of MLR properties). If finding independent information is the central aim, then one might look for long term trends in alkalinity. That would be a totally different study, with an objective different from ours (investigating pH trends from observations). There are processes other than pH change that can affect alkalinity. This variable responds linearly to mixing and, arguably, remineralization, and would therefore be a better choice for MLR analysis. It is also more orthogonal to C_T with respect to the carbonate system, and therefore would contain more independent information than pH given that trends in C_T have already been documented. Given the authors' assumptions of constant alkalinity, temperature, and salinity, and given the findings of Pérez et al., [2010], the main findings of this paper simplify to "all other things being equal, seawater pH decreases when C_T increases." Please, refer to the new discussion section and to previous answers (point 4 on the general comments in the first page of this letter). There are processes other than C_{ant} influence that affect the obtained pH trends, and this is examined and discussed.

On a final note, the statistical requirements for demonstrating that observed trends are indeed the result of long-term (relative to the length of the timeseries) trends rather than decadal variability are steep. See a paper by Weatherhead et al. [1998] for in-depth analysis of what is required to demonstrate the presence of a long-term trend. Until such considerations have been taken into account, this discussion should be rephrased to allow for the possibility that the trends observed are the results of decadal variability in the relationships between the tracers used. The tone of the revised discussion section goes more along these lines and allows for such possibility. However, given the aforementioned arguments, we believe there is no evidence for such possibility. In summary, and as mentioned in many of the above comments, there are no funded reasons that support the existence of biases in the trends, mainly because of the following: 1) All of the data here used have passed the 2QC of the CARINA dataset; and 2) The noise and "biases" in the INADW, which is the most isolated water mass in this study, consistently showed an average pH of 7.727 ± 0.004 , with no statistically significant signs of pH variation between 1981 and 2008, for all 13 cruises used in our study. In addition, having done the data analysis taking the main water masses in the NASPG as "analytical cells or units", with homogeneous properties, gives robustness to the results and largely avoids potential non-linearities in the analysis and in the trends.

Specific Comments

GENERAL COMMENT: Given that the manuscript has changed substantially (motivated by the comments), a lot of these comments no longer apply since the sentences to which they refer have been fully removed or changed. However, we will answer all of them here to make easier for the reviewer keeping track of all of the changes in the new version (attached at the end of this reply letter).

Format: Page Number.Line Number – “Text being commented upon” Comment

3004.13 – “Unprecedented” This is a strong word that would require justification that is beyond the scope of this paper. Thank you. You are right. We have deleted this word. We now simply say on the abstract that: “...*The highest rates were associated with surface waters and with Labrador Seawater (LSW)*...”.

3004.14 to 15 – “The latter ... water mass.” This sentence only makes sense after the next sentence is read. This has been changed: “...*The deep convection activity in the North Atlantic Subpolar Gyre injects surface waters loaded with anthropogenic CO₂ into lower layers, provoking the remarkable acidification rate observed for LSW in the Iceland basin of -0.0016±0.0002 yr⁻¹.*”.

3004.18 – “Lineal” Should be linear. Done.

3005.5 – “30% reduction in pH.” Should be “30% reduction in [H+].” Done.

3005.11 – “medley of juxtaposed” This is confusing. We changed it to: “...*Ocean acidification causes a combination of contrasted impacts on the marine environment (Doney et al., 2009), from reproductive larval survivorship and growth-related issues in several taxa to the reduction of seawater’s sound absorption coefficient (Ilyina et al., 2009).*”.

3005.16 to 19 – “It has ... capacity.” This is misleading since it implies that the same amount of CO₂ is being added everywhere. The *p*CO₂ of the atmosphere is changing, and regions with higher Revelle factors will change their C_T less in response to a change in *p*CO₂. It would perhaps be best to simply mention that at high Revelle factors, a given change in *p*CO₂ will produce a larger change in pH. We have changed this entire focus of this paragraph to introduce readers to the aspects of the NASPG that are more relevant to our study and are later discussed more fully. Here is the new version: “...*The North Atlantic Subpolar Gyre (NASPG) is an important area of mode waters formation. These waters formed in deep winter mixed layers are identified by nearly uniform properties in the vertical near the top of the permanent pycnocline (Thierry et al., 2008). The process of transformation of the warm, saline subtropical waters into intermediate and deep waters in the NASPG (McCartney and Talley, 1982; Read, 2001) results in several varieties of Subpolar Mode Water (SPMW) distributed around the gyre. The Labrador Sea Water (LSW), the densest variety of SPMW, is one of the thickest water masses in the NA and one of the main components of the lower limb of the Meridional Overturning Circulation (Thierry et al., 2008). The LSW has high contents of chlorofluorocarbons (CFCs) and anthropogenic carbon due to the ventilation processes (Azetsu-Scott et al., 2003; Pérez et al., 2010). Thus, it is expected that those water masses will suffer changes in [H⁺].*”. However, the most ecologically relevant quantity, the change in the saturation of calcite or aragonite, is actually smaller for a given change in *p*CO₂ in colder higher-Revelle-factor waters. We have removed all discussion and most references to the ecological impacts of ocean acidification to focus on the elements that were directly more relevant to the main objective of the study, i.e., quantify the pH evolution in the main water masses of the NASPG during the last three decades.

3005.24 to 27 – “The negative feedback is that as... 2010).” This sentence needs rewriting, I believe. Following from the answer to the previous comment, we have deleted this sentence, for the same reasons explained above.

3006.3 and 15 – “synthetic ocean data” Synthetic should be replaced: e.g. “and ocean data syntheses (or an ocean data synthesis).” By “synthetic ocean data” we meant data from numerical models. We have changed it: “...*Several past and future pH projections have been proposed from Ocean General Circulation Models (GCMs) and model data (Orr et al., 2005)...*”. The second occurrence (on line 15) has been removed in the revised version.

3007.13 – “precision limits of 0.002 pH units.” The excellent precision of spectrophotometric pH measurements is only a fringe benefit for this study (by perhaps reducing the random noise around your regressions). It is important to note that the large accuracy problems for past pH measurements can greatly complicate trend detection. Please, refer to the answers given in the “Scientific comments” section above.

3008.1 to 2 – “The estimated... is ± 0.0034 .” This comment requires justification. We have changed it: “...*Some of the cruises listed in Table 1 did not perform direct pH measurements but obtained total alkalinity (A_T) and dissolved inorganic carbon (C_T) data. In such cases the pH values were calculated in the SWS scale from A_T and C_T data using the thermodynamic equations of the carbon system (Dickson et al., 2007) and a set of CO_2 dissociation constants (Dickson and Millero, 1987). The pH estimated accuracy ranges from ± 0.002 to ± 0.008 depending of the used methodology at each cruise (Table 1).*”.

3009.16 to 19 – “To be consistent ... whenever possible.” Why not neutral density... simply for compatibility? The selected isopycnals delimit the main water masses in the NASPG. In addition, by using the same isopycnal layers as in Pérez et al. 2010 we could use the C_{ant} storage rate data they provide and use it to compare our acidification rates with the pH rates expected from C_{ant} influence, and this is an added value to the discussion. What are the limits used? Where was using the cited proposed limits not possible and why? How sensitive are the results to the choice of limits? Please note that former section 2.2.1 has been deleted. The description of the isopycnals selected to delimit the main water masses in the NASPG, as well as the works on which we based our decisions for choosing those limits, is now provided on the second paragraph of section 2.2 (and also in Fig. 1b and 2).

3010.Paragraph 1 – This paragraph is vague. It is not clear what is meant by “considering the signature” until the next paragraph, and there is no indication that the signature considered should be that of a process that changes pH linearly. We have removed this paragraph.

3012. 14 to 18 – “Deeper and older... organic matter.” As written, this implies that pH is lower because there are lower oxygen concentrations. You are right. We changed it to: “...*The general pattern of pH_{SWS25} follows the natural distribution expected, with higher pH values at the surface and lower pH in deep waters: The high values of pH_{SWS25} above the seasonal thermocline, in the photic layer (uppermost ~400 m), respond to the photosynthetic activity of primary producers that withdraw dissolved CO_2 from seawater. The deep and less ventilated NADW has low pH_{SWS25} .*”.

3013.23 to 29 – “To estimate the acidification... surface ocean.” This paragraph is very vague about what was done. We did not want to repeat what had been described in section 2.2 all over again and thus just listed the calculations that were done in order to obtain the trends plotted in Fig. 3. We have made this more explicit on the revised version: “...*To estimate the acidification rates of the water masses we normalised the discrete in situ pH_{SWS25} data to basin-average conditions ($pH_{SWS25-BA}$), as described on section 2.2.*”. Also, it is not clear that all natural variability was removed. If a long term trend in pH were occurring naturally, would your methods have removed it successfully? If yes, how would it not have also removed any anthropogenic trend? Concerning this, please, refer again to point 1) in the general comments on the first page of this letter. The methodology described in section 2.2 does not aim at separating the anthropogenic and the natural acidification signals; it is just a normalization of the average pH (per layer and basin) to the average basin conditions.

3014.13 – “specific alkalinity.” “Alkalinity” would make more sense here, I believe. The sentence has changed to: “...*The MW in the ENA basin showed a moderate acidification rate ($-0.0006 \pm 0.0001 \text{ yr}^{-1}$) due to its known capacity for C_{ant} drawdown by entrainment from surface layers (Ríos et al., 2001; Álvarez et al., 2005).*”.

3015.8 – “such trend appears.” The language is off here. This sentence has been deleted in the revised manuscript version.

3015.8 to 9 – “rapidly formed upper LSW (uLSW) meant...” The language is off here. It implies the water meant something. It has been corrected (penultimate paragraph in the Discussion section): “...*The rapid subduction of this newly formed cLSW injected C_{ant} from surface to intermediate waters, transporting C_{ant} much faster than via downward diffusion alone, thus causing a faster acidification rate in the cLSW (where organic matter remineralization also contributes significantly to the pH lowering) than in the SPMW, where C_{ant} influence is the main contributor to acidification.*”.

3015.20 to 23 – “In summary... faster than it would occur...” Is this a new result? If not, should it not be put in the context of other papers with similar findings for this and other water masses. No, it is not a new result. It is a hypothesis (based on NASPG circulation, ventilation and C_{ant} storage) to explain the obtained results regarding the fast acidification and aragonite undersaturation of cLSW in the future (according to our projections). The paragraph has moved and is now the penultimate one in the Discussion section. We have also rephrased the explanation: “...*The high-NAO enhanced ventilation that occurred towards the mid-late 1980s fostered the fast formation of a massive cLSW vintage (Kieke et al., 2007; Yashayaev et al., 2008). The rapid subduction of this newly formed cLSW meant an injection of C_{ant} from surface to intermediate waters, transporting C_{ant} much faster than via downward diffusion alone, thus causing a faster acidification rate in the cLSW (where organic matter remineralization also contributes significantly to the pH lowering) than in the SPMW, where C_{ant} influence is the main contributor to acidification...*”.

3015.24 – “plausible” This should be “possible.” Done. Also, please note that the corresponding paragraph (fourth paragraph on the Discussion section) has notably changed.

3017.14 – “worst-case” This scenario name will likely be clear to Earth scientists, but perhaps be more specific here. Motivated by this type of confusion, we have deleted the references to the two CO_2 emission scenarios we mentioned in the manuscript to avoid complicating the main message. Our projections are based on $x\text{CO}_2$ values, not on time, or on how fast those $x\text{CO}_2$ values are reached (that depends on the emission rate / scenario). The reason we included the emission scenarios was to provide some context, but this seemed to blur the main message, so we decided to omit these references.

3018.4 to 7 “The shoaling of the ... lysocline shoaling.” I was unsure what was meant by this or how this conclusion was reached from the data presented. Thank you for this comment. This was a little confusing and misleading, as you point out. We have deleted this sentence.

Observed acidification trends in North Atlantic water masses

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Abstract

The lack of observational pH data has made difficult assessing recent rates of ocean acidification, particularly in the high latitudes. Here we present a time series that spans over 27 years (1981-2008) of high-quality carbon system measurements in the North Atlantic that comprise fourteen cruises and cover the important water mass formation areas of the Irminger and Iceland basins. We provide direct quantification of acidification rates in upper and intermediate North Atlantic waters. The highest rates were associated with surface waters and with Labrador Seawater (LSW). The Subarctic Intermediate and Subpolar Mode waters (SAIW and SPMW) showed acidification rates of -0.0019 ± 0.0001 and $-0.0012 \pm 0.0002 \text{ yr}^{-1}$, respectively. The deep convection activity in the North Atlantic Subpolar Gyre injects surface waters loaded with anthropogenic CO_2 into lower layers, provoking the remarkable acidification rate observed for LSW in the Iceland basin of $-0.0016 \pm 0.0002 \text{ yr}^{-1}$. An extrapolation of the observed acidification linear trends suggests that the pH of LSW could drop 0.45 units with respect to pre-industrial levels by the time atmospheric CO_2 concentrations reach ~ 775 ppm. Under similar circulation conditions and evolution of the CO_2 emission rates to the ones during the last three decades, the $c\text{LSW}$ in the Iceland basin could become undersaturated in dissolved aragonite earlier than the surface SPMW, by the time atmospheric CO_2 reaches 550 ppm.

1. Introduction

The ocean acidification due to the increasing atmospheric CO₂ is well known (Doney et al., 2009; Raven et al., 2005) but the direct pH observations are sparse (Byrne et al., 2010; Tittensor et al., 2010; Wootton et al., 2008). Roughly 20-35% of the anthropogenic CO₂ (C_{ant}) emissions are absorbed by the oceans (Khaliq et al., 2009) mitigating the global warming. Since the beginning of the Industrial Revolution the sea-surface has seen a 30% increase in hydrogen ion concentrations [H⁺] (Caldeira and Wickett, 2005; Raven et al., 2005). The current acidification episode is occurring ~100 times faster than any other acidity change in the last 50 million years of Earth's history (Pelejero et al., 2010), and is thought to be the onset for a number of cascading effects throughout marine ecosystems that may leave no time for adaptation of many organisms (Feely et al., 2008; Doney et al., 2009). Ocean acidification causes a combination of contrasted impacts on the marine environment (Doney et al., 2009), from reproductive larval survivorship and growth-related issues in several taxa to the reduction of seawater's sound absorption coefficient (Ilyina et al., 2009).

The North Atlantic Subpolar Gyre (NASPG) is an important area of mode waters formation. These waters formed in deep winter mixed layers are identified by nearly uniform properties in the vertical near the top of the permanent pycnocline (Thierry et al., 2008). The process of transformation of the warm, saline subtropical waters into intermediate and deep waters in the NASPG (McCartney and Talley, 1982; Read, 2001) results in several varieties of Subpolar Mode Water (SPMW) distributed around the gyre. The Labrador Sea Water (LSW), the densest variety of SPMW, is one of the thickest water masses in the NA and one of the main components of the lower limb of the Meridional Overturning Circulation (Thierry et al., 2008). The LSW has high contents of chlorofluorocarbons (CFCs) and anthropogenic carbon due to the ventilation processes (Azetsu-Scott et al., 2003; Pérez et al., 2010). Thus, it is expected that those water masses will suffer changes in [H⁺].

There are relatively few places where the carbon system has been surveyed thoroughly enough to generate a comprehensive database that can be used in the assessment of ocean acidification and its environmental impacts (Wootton et al., 2008). Several past and future pH projections have been proposed from Ocean General Circulation Models (GCMs) and model data (Orr et al., 2005), but *in situ* measurements documenting the evolution of ocean pH over time are limited (Wootton et al., 2008). The present work examines the temporal variability of pH in the main water masses of the North Atlantic from direct observations. Here we have gathered the available high-quality carbon system data covering the NASPG between 1981 and 2008 (Fig. 1a) to study the decadal acidification rates of the main North Atlantic water masses (Fig. 1b) during that time period.

2. Dataset and methodology

2.1 Dataset

A total of fourteen cruises with high-quality carbon system measurements were selected to follow the temporal evolution of pH in the North Atlantic (Fig. 1a, Table 1). Cruise data can be accessed at CARINA site <http://store.pangaea.de/Projects/CARBOOCEAN/carina/index.htm>. The climatological WOA05 data is available at http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html.

Over time, different analytical procedures were used to measure pH and so different adjustments and corrections were applied to the raw data to create the pH dataset used in this study (Table 1). The pH measurements in the database were determined either potentiometrically (using pH electrodes; Dickson, 1993) or, more commonly, with a spectrophotometric method that used *m*-cresol purple as a pH indicator in either scanning or diode array spectrophotometers (Clayton and Byrne, 1993). The spectrophotometric pH determination has typical reported precision limits of 0.002 pH units (Clayton and Byrne, 1993; Millero, 2007). Periodical checks of pH measurement precision with Certified Reference Material (CRM) during the FOUREX and OVIDE cruises

indicated a precision better than the 0.002 pH units reported by Clayton and Byrne (1993) and Millero (2007). All pH measurements that had not been originally reported in the seawater scale (pH_{SWS} ; Millero, 2007) were converted to it from either the total or the NBS pH scale using the corresponding acid dissociation constants (Dickson and Millero, 1987), following the CARINA database second quality control recommendations for pH data scale unification and cruise adjustments (Velo et al., 2010). The acid dissociation constants for HF or HSO_4^- (Millero, 2007) were used to convert pH values originally reported in the total scale (those measured spectrophotometrically; Table 1) to the SWS scale. The pHs measured potentiometrically were all reported on the NBS scale and were converted to the SWS scale as specified in Pérez and Fraga (1987). Some of the cruises listed in Table 1 did not perform direct pH measurements but obtained total alkalinity (A_T) and dissolved inorganic carbon (C_T) data. In such cases the pH values were calculated in the SWS scale from A_T and C_T data using the thermodynamic equations of the carbon system (Dickson et al., 2007) and a set of CO_2 dissociation constants (Dickson and Millero, 1987). The pH estimated accuracy ranges from ± 0.002 to ± 0.008 depending of the used methodology at each cruise (Table 1).

During the A16N cruise, pH was determined spectrophotometrically, but the spatial resolution was not as good as than for C_T and A_T , so we used pH values calculated from C_T and A_T for this cruise instead. The AR7E and A01E cruises (Fig. 1a) had comprehensive amount of C_T measurements yet very few potentiometric A_T data. Given the scarcity of A_T data, the equation $A_T = S/35 \cdot (2294.7 + 1.37 [\text{Si}(\text{OH})_4])$ ($R^2=0.97$; $[\text{Si}(\text{OH})_4]$ refers to silicate concentration) given by Pérez et al. (2010) was applied to the AR7E and A01E datasets to generate A_T values at the sampling depths of measured C_T . The pH was then calculated from C_T and A_T data as mentioned above.

2.2 pH data analysis

The dataset spans 27 years (1981-2008) with a wide spatial coverage of the study area (Fig. 1a; Table 1) that was divided in three basins: Irminger, Iceland and East North Atlantic (ENA).

These three basins and their geographical boundaries were defined by Pérez et al. (2010). So for the Irminger basin, the boundaries are defined by the main axis of the Reykjanes Ridge and the east coast of Greenland. The Iceland basin was defined as the region bounded between the Reykjanes Ridge axis and the line joining the Eriador Seamount and the Faroe Islands. The ENA basin extends south from Eriador-Faroe line over the Rockall through, the Porcupine bank, and the Biscay and Iberian basins (Fig. 1).

In order to evaluate the temporal variability of the pH in the water masses of the North Atlantic, the water column was divided in five layers by potential density (σ_θ) intervals for each region (Fig. 1b). To determine the isopycnals boundaries of the North Atlantic Deep Water (NADW) we followed Lherminier et al. (2010), who established different layers by potential density intervals on the basis of the hydrographic properties and circulation of the different water masses along the OVIDE section. They discriminate between the two components of NADW: the lower NADW (*l*NADW) spreading from the bottom to $\sigma_\theta = 45.84 \text{ kg m}^{-3}$ and the upper NADW (*u*NADW) spreading in the density range $36.94 < \sigma_\theta < 45.84 \text{ kg m}^{-3}$. We took the density range $37 < \sigma_\theta < 45.84 \text{ kg m}^{-3}$, which is almost identical, because the isopycnal $\sigma_\theta = 37$ seemed to delimit better the deepest boundary of the *c*LSW core (coincident with the *u*NADW upper density limit) in the Iceland and ENA basins. For the spreading of LSW in the ENA basin, the density range selected ($32.35 < \sigma_\theta < 37 \text{ kg m}^{-3}$) is very close to the Lherminier et al. (2010). Following Ríos et al. (1992) the Mediterranean Water (MW) layer is delimited by $27.2 < \sigma_\theta < 32.35 \text{ kg m}^{-3}$ and the North Atlantic Central Water (NACW) layer is established from surface to $\sigma_\theta < 32.35 \text{ kg m}^{-3}$ according to the spreading of these water masses in the zone. For the Irminger and Iceland basins, the potential density limits were established following Kieke et al. (2007) and Yashayaev et al. (2008). So, for the Iceland basin the layer of Sub Polar Mode Water (SPMW) is found between 100 m and $\sigma_\theta = 27.6 \text{ kg m}^{-3}$. The upper and classical LSW (*u*LSW and *c*LSW) spread in the density ranges of $27.68 < \sigma_\theta < 27.76 \text{ kg m}^{-3}$ and $27.76 < \sigma_\theta < 27.81 \text{ kg m}^{-3}$, respectively. For the Irminger basin the Sub Arctic Intermediate Water (SAIW) spreads from 100 m to 27.68 kg m^{-3} , the *u*LSW and *c*LSW are

found between $27.68 < \sigma_\theta < 27.76 \text{ kgm}^{-3}$; between $27.76 < \sigma_\theta < 27.81 \text{ kgm}^{-3}$, respectively. The North Atlantic Deep Water (NADW, which includes the ISOW contributions) is delimited by $27.81 < \sigma_\theta < 27.88 \text{ kg m}^{-3}$, and the Denmark Strait Overflow Water (DSOW) by $\sigma_\theta > 27.88 \text{ kg m}^{-3}$ (Fig. 1b).

2.2.1 Basin normalization of average pH_{SWS25}

The average pH_{SWS25} was obtained for each layer at each year and for the three basins, following the averaging and “basin-referencing” methodology that Pérez et al. (2008, 2010) and Ríos et al. (2012) used for C_{ant} . The spatial coverage of each year is variable and this can cause significant biases in the observed average layer properties in each year. These small differences can potentially introduce spatial biases in the average pH_{SWS25} due to different ventilation stages and rates of each water mass. Therefore, for each basin the pH_{SWS25} were normalized to better represent the pH_{SWS25} in each considered layer of the basin (Fig. 1) by adding a new term named as $\Delta\text{pH}_{\text{SWS25-BA}}$. This term represents the deviation of the pH_{SWS25} (average from cruise data) from the $\text{pH}_{\text{SWS25-BA}}$ basin average (BA).

$$\text{pH}_{\text{SWS25-BA}} = \text{pH}_{\text{SWS25}} + \Delta\text{pH}_{\text{SWS25-BA}} \quad (1)$$

The $\Delta\text{pH}_{\text{SWS25-BA}}$ term was computed from cruise data and expressed as individual correction elements for each cruise and layer in the three basins as follows:

$$\Delta\text{pH}_{\text{SWS25-BA}} = \sum_{i=1}^4 a_i (X_i^{\text{WOA05}} - X_i^c) \quad (2)$$

Where “c” stands for “cruise” and subscript “i” denotes “property” (1=Si(OH)₄; 2=AOU; 3=θ; 4=S). The “ X_i^c ” and “ X_i^{WOA05} ” terms are the average magnitudes of the “ith” properties from direct observations along the cruise track and from WOA05 data in the whole basin, respectively (Table 2). The “ a_i ” factors are the regression coefficients that were calculated in each basin for each layer from a multiple linear regression (MLR) fit (Equation 3) of the pH_{SWS25} averages vs. the averaged

“ i ” properties using data from the fourteen cruises (Table 2). The obtained “ a_i ” regression coefficients are listed in Table 3.

$$\text{pH}_{\text{SWS25}}^{\text{MLR}} = \sum_{i=1}^5 a_i X_i^c + k \quad (3)$$

All terms and scripts in equation (3) have the same meaning as in equation (2). Also, the X_i^c terms for $i=1$ through 4 are the same as in equation (2). The same is true for the a_i coefficients in equation (2). Actually, the purpose of equation (3) is obtaining those a_i values to be used in equation (2). The $X_5 = x\text{CO}_2^{\text{atm}}$ values used as input parameters in equation (3) are the averages for the year of the corresponding cruise “ c ”. The $x\text{CO}_2^{\text{atm}}$ records were obtained from time series from meteorological stations in the NASPG (Storhofdi (Iceland); CIBA (Spain); Mace Head (Ireland); Ocean Station C (U.S.); Pico-Azores (Portugal); and Terceira Island-Azores (Portugal)), that are part of the global cooperative air-sampling network managed and operated by the National Oceanic and Atmospheric Administration (NOAA) Carbon Cycle Greenhouse Gas group (<http://www.esrl.noaa.gov/gmd/ccgg/flask.html>). The a_5 term associated with the $x\text{CO}_2^{\text{atm}}$ variable (Table 3) in equation (3) is not used in equation (2) since the $\Delta\text{pH}_{\text{SWS25-BA}}$ term should only include the effect of variables with spatial variation. Such $x\text{CO}_2^{\text{atm}}$ terms are required when calculating the “ a_i ” coefficients (equation 3, Table 3), since $x\text{CO}_2^{\text{atm}}$ has co-variation with $\text{pH}_{25\text{SWS}}$. By including “ a_5 ” in equation (3) we remove from the rest of “ a_i ” factors the transient influences that co-vary with pH_{SWS25} . Considering that pH varies with the time because of the $x\text{CO}_2$ change, the inclusion of this variable in the eq. 3 assures that coefficients of the other properties that change mostly spatially are more consistent than if the $x\text{CO}_2^{\text{atm}}$ is not included.

3. Results

The vertical distributions of pH_{SWS25} measured along the section between the Iberian Peninsula and Greenland are shown in Figure 2, providing a first look at the evolution of pH over

the last two decades. The general pattern of pH_{SWS25} follows the natural distribution expected, with higher pH values at the surface and lower pH in deep waters: The high values of pH_{SWS25} above the seasonal thermocline, in the photic layer (uppermost ~ 400 m), respond to the photosynthetic activity of primary producers that withdraw dissolved CO_2 from seawater. The deep and less ventilated NADW has low pH_{SWS25} . The NADW is located generally below 2500 dbar ($\sigma_2 > 37.00$ kg m^{-3} ; Fig. 1b) mainly in the deep ENA basin and shows weak signs of acidification over the last two decades, although there exist slight differences between the upper and lower NADW branches (*u*NADW and *l*NADW). The branch of *u*NADW that spreads westward into the Iceland basin mixes with LSW (Yashayaev et al., 2008) forming a pH gradient that shows decreasing pH values over time. The influence of LSW in the *u*NADW is also revealed by the imprint of LSW in the AOU and $\text{Si}(\text{OH})_4$ values of the *u*NADW, which are lower than those in the *l*NADW layer (Table 2c). In the Irminger basin the decreasing trends of pH_{SWS25} are clearly visible in the most recently ventilated waters like the *u*LSW and DSOW (Fig. 2). The latter shows low pH_{SWS25} in 2004 and 2008 and higher values in 2006 due to the different NAO conditions (Pérez et al., 2010). The most evident sign of acidification is detected between 1000 and 2000 meters depth, where the volume of water with pH values below 7.725 thickens over time.

To estimate the acidification rates of the water masses we normalised the discrete *in situ* pH_{SWS25} data to basin-average conditions ($\text{pH}_{\text{SWS25-BA}}$), as described on section 2.2. The correction applied ($\Delta\text{pH}_{\text{SWS25-BA}}$) is, on average, 0.003 ± 0.009 in the studied region (Table 2). On average, the largest corrections correspond to the Irminger basin (0.007 ± 0.009), while in the Iceland and ENA basins they are smaller (0.003 ± 0.009 and 0.002 ± 0.010 , respectively). In the Irminger basin no correction was applied to the *u*NADW and DSOW layers (Table 2a). The highest average corrections on this basin were applied to the *u*LSW (0.014 ± 0.008) and *c*LSW (0.012 ± 0.005) layers, and the highest individual correction (0.027 ± 0.003) corresponds to the SAIW in 1997. The smallest average $\text{pH}_{\text{SWS25-BA}}$ corrections in the Iceland basin correspond to the *u*LSW (0.000 ± 0.003) and the

largest to the SPMW layer (0.008 ± 0.014), to which also the highest individual correction was applied (0.003 ± 0.005) corresponding to the 1991 A01E cruise. In the ENA basin the smallest average corrections correspond to LSW and NACW layers (0.0012 ± 0.004 and 0.0045 ± 0.004 , respectively) and the largest to the MW (0.014 ± 0.002), where the highest individual corrections were also applied (0.023 ± 0.002), in 1998 and 2003, to the cruises conducted along 20°W . In general, we can see a trend of decreasing pH over time for both pH_{SWS25} and $\text{pH}_{25\text{SWS-BA}}$ in all basins and layers (Table 2). These decreasing pH_{SWS25} trends tend to be more pronounced in the Irminger and Iceland basins and less marked in the ENA basin (Table 2). The SAIW and μLSW layers in the Irminger basin show a strong decreasing pH_{SWS25} trends in the period 1981 to 1997 (positive NAO index) and less pronounced ones from 2002 to 2008. In the deepest layers ($c\text{LSW}$, μNADW and DSOW) the pH_{SWS25} trends are lower although there is also a minimum value in 1997 when the NAO phase changes from positive to neutral/negative. Similar pH_{SWS25} trends are observed in the Iceland basin with a noticeable decrease from 1981 to 1997 during the high NAO followed of a slow decreasing pH_{SWS25} values. Differently, in the ENA basin the lowering pH_{SWS25} shows a more continuous trend with a maximum during 1981 and the minimum in 2006 in the NACW and LSW layers. Also at the ENA basin, the μNADW and NADW show rather constant pH_{SWS25} values, with no clear trends. The pH_{SWS25} signal in the MW layer is noisier due to the important variations in salinity caused by the mixing between MW and other water masses, and as a consequence of the change in cruise tracks throughout the considered time period.

The evolution of the average $\text{pH}_{\text{SWS25-BA}}$ between 1981 and 2008 in each layer and basin is plotted in Figure 3. The error bars on the graph represent the error of the mean and the uncertainty due to the normalization of the data. The general pattern is that the acidification rates tend to decrease with depth in all basins. The lowest slopes are found in the ENA basin, and the fastest acidification rates correspond to recently ventilated waters like the SAIW ($-0.0019 \pm 0.0001 \text{ yr}^{-1}$) and the μLSW ($-0.0017 \pm 0.00004 \text{ yr}^{-1}$) (both in the Irminger basin), and the SPMW ($-0.0012 \pm 0.0002 \text{ yr}^{-1}$)

¹) in the Iceland basin. The $\text{pH}_{\text{SWS25-BA}}$ of *c*LSW in the Iceland basin presents a remarkable average decrease of $-0.0016 \pm 0.0002 \text{ yr}^{-1}$, unlike in the Irminger and ENA basins (-0.00089 ± 0.00004 and $-0.0008 \pm 0.0001 \text{ yr}^{-1}$, respectively). The layer of *u*NADW shows decreasing $\text{pH}_{\text{SWS25-BA}}$ vs. time trends from the Irminger ($-0.0010 \pm 0.0001 \text{ yr}^{-1}$) to the Iceland basin ($-0.0008 \pm 0.0002 \text{ yr}^{-1}$) due to the influence of ISOW and to the mixing with LSW. Overall, the *l*NADW and *u*NADW in the ENA basin are the least acidified water masses over time, with low $\text{pH}_{\text{SWS25-BA}}$ vs. time slopes. These latter two regression fits are, in addition, statistically non-significant (both p-values > 0.2) and show low pH-time correlation: $0.0002 \pm 0.0002 \text{ yr}^{-1}$ ($R^2 = 0.15$; p-value = 0.57) and $-0.0003 \pm 0.0001 \text{ yr}^{-1}$ ($R^2 = 0.28$; p-value = 0.47) for *l*NADW and *u*NADW, respectively. The MW in the ENA basin showed a moderate acidification rate ($-0.0006 \pm 0.0001 \text{ yr}^{-1}$) due to its known capacity for C_{ant} drawdown by entrainment from surface layers (Ríos et al., 2001; Álvarez et al., 2005).

4. Discussion

The acidification of the upper layer NASPG waters here assessed from *in situ* pH measurements spanning the last three decades (1981 to 2008) shows very similar tendencies of pH decline to those observed in the time series stations ESTOC ($29^{\circ}10'N$, $15^{\circ}30'W$) and BATS ($31^{\circ}43'N$, $64^{\circ}10'W$), in the Subtropical Atlantic. At the Irminger basin, the observed values of $\text{pH}_{\text{SWS25-BA}}$ decrease rates for SAIW and *u*LSW are -0.0019 ± 0.0002 and $-0.0017 \pm 0.0001 \text{ yr}^{-1}$, respectively, similar to those obtained by Olafsson et al. (2009) for surface waters during the winter (0.0024 yr^{-1}). The slight difference with the values reported by Olafsson et al. (2009) likely comes from the fact that the surface isopycnals here considered include thick layers of mode waters with lower interannual variations. The acidification rates here obtained for SAIW and *u*LSW in the Irminger basin are also comparable to those reported in the Subtropical North Atlantic at the ESTOC site in surface waters and in the mixed layer (-0.0017 yr^{-1}) during the decade 1995-2004 (Santana-Casiano et al., 2007; González-Dávila et al., 2010), and at the BATS site in surface waters

(-0.0016 yr^{-1}) from 1983 to 2011 (Bates et al., 2012). In the ENA basin, the $\text{pH}_{\text{SWS25-BA}}$ decreasing rate of the NACW ($-0.0009 \pm 0.0001 \text{ yr}^{-1}$) is similar to the rates computed at the ESTOC site at 300 and 600 m (-0.0010 ± 0.0004 and $-0.0008 \pm 0.0003 \text{ yr}^{-1}$, respectively) for the decade 1995-2004 (González-Dávila et al., 2010). At 3500 m, the $\text{pH}_{\text{SWS25-BA}}$ rate of decrease for INADW here obtained ($0.0002 \pm 0.0002 \text{ yr}^{-1}$) has a very low pH vs. time correlation coefficient ($r^2=0.15$; Fig. 3c) and is therefore not significant, yet similar to that given by González-Dávila et al. (2010) ($-0.0002 \pm 0.0002 \text{ yr}^{-1}$) for the same water mass between 1995 and 2004. On the contrary, at the layer where the MW spreads around 1000 m, González Dávila et al. (2010) reported a pH decreasing rate ($-0.0008 \pm 0.0003 \text{ yr}^{-1}$) slightly higher (considering the associated uncertainties) than our pH rate ($-0.0006 \pm 0.0001 \text{ yr}^{-1}$) for this water mass. The difference could be due to the way MW is defined in our work compared to González-Dávila et al. (2010), were they consider MW as the mix of at least three different water types (including MW, Antarctic Intermediate Water and NACW) at the east North Atlantic (González-Dávila et al., 2010).

Ocean uptake and chemical equilibration of C_{ant} with seawater results in a gradual reduction of seawater pH and saturation rates (Ω) for calcium carbonate (CaCO_3) minerals in a process termed ocean acidification (Bates et al., 2012). However, other contributions to these pH reductions such as ventilation of the water masses or remineralization of organic matter exist. We have checked if the here obtained $\text{pH}_{\text{SWS25-BA}}$ decrease rates follow the expected trends due mainly to C_{ant} uptake using the C_{ant} rates given by Pérez et al. (2010). The necessary pHs to obtain such rates were calculated using the expression $(\partial \text{pH} / \partial t)_{\text{ANT}} = (\partial C_{\text{ANT}} / \partial t)(\partial \text{pH} / \partial C_{\text{T}})_{(\text{S}, \text{A}_\text{T})}$, where $(\partial \text{pH} / \partial t)_{\text{ANT}}$ is the expected variation over time of human-induced pH (due to C_{ant}); $(\partial C_{\text{ANT}} / \partial t)$ is the corresponding C_{ant} storage rate (from Pérez et al., 2010); and $(\partial \text{pH} / \partial C_{\text{T}})_{(\text{S}, \text{A}_\text{T})}$ is the variation with respect to C_{T} of the pH calculated from the thermodynamic equations of the marine inorganic carbon system (as described in section 2), using the available A_{T} data and salinity measurements.

The $\text{pH}_{\text{SWS25-BA}}$ decrease of the layers *c*LSW, *u*NADW and DSOW (Irminger basin), and SPMW and *u*NADW (Iceland basin) do follow the expected trend due to C_{ant} entry. However, there are some deviations from this pattern in the rest of the considered water masses. In the layers of *u*LSW (Irminger and Iceland basins) and *c*LSW (Iceland basin) there is a component (~50%) of the observed acidification trends that is not explained by the uptake of C_{ant} and is attributed organic matter remineralization. The SAIW layer in the Irminger basin presents an intermediate case compared to the previous ones: ~75% of the $\text{pH}_{\text{SWS25-BA}}$ decrease comes from the influence of C_{ant} . In contrast with the observed in the Irminger basin, in the upper layer of the ENA basin the acidification due to the increase of C_{ant} is partially compensated by the increase in ventilation (and, consequently, higher CO_2 removal via the enhanced photosynthetic activity) of the eastern NACW (ENACW) that produces lower acidification rates than expected.

From our set of $\text{pH}_{\text{SWS25-BA}}$ observations we have made projections of future pH levels (Fig. 4). The Iceland basin is particularly suitable for extrapolating the pH trends from Fig. 3b into the future given the good coverage of measurements available in this region, as this would confer added robustness to the projected acidification trends. The SPMW and *c*LSW are selected for such projections, because they are some of the most susceptible of the considered water masses to human-induced acidification and also have strong pH vs time fits (Fig. 3b). The projections are calculated under the assumption that the observed acidification trends shown in Fig. 3 and the ocean's general circulation for the rest of the 21st century remain similar to those observed during the last three decades.

The strength and phase of the NAO index affect water mass ventilation and C_{ant} uptake rates (Pérez et al., 2010). However, the fact that the NAO phase was close to neutral both in the 1980s and 2000s should minimise potential biases in the proposed linear projections of pH, which are based on observations from the results here obtained (Fig. 3). Although such linear extrapolation is not constrained, several works have demonstrated that the decline of carbon system parameters like $[\text{CO}_3^{2-}]$ is almost linear for predictions made between 2000 and 2050 (Zeebe and Wolf-Gladrow,

2001; Hauck et al., 2010). The buffering effect of carbonate minerals and biogenic CaCO_3 dissolution can be disregarded since these processes tend to occur in deep waters over timescales that are at least one order of magnitude larger than the one here considered. We therefore assume analogous pH evolution to the one here observed in surface (SPMW) and intermediate (*c*LSW) waters on decadal timescales (our observational time span), which is the time frame in which the atmospheric CO_2 concentration range considered in Fig. 4 is expected to be reached under a business-as-usual CO_2 emission scenario.

Concerning the assumption of general circulation there is the caveat that the increased stratification of surface layers expected in the future (Friedlingstein and Prentice, 2010) can hamper water mass ventilation processes and potentially bring about a decrease of pH (acidification), because C_{ant} would not be as effectively transported toward the ocean interior via deep convection and water mass formation processes (Pérez et al., 2010). Therefore, if such increased stratification prediction holds true in the future, assuming a steady state for the general circulation can potentially cause overestimates in the pH values of the linear projections for surface and intermediate waters from Fig. 4. Nevertheless, this process of slowing acidification due to less C_{ant} entry could be counterbalanced by the increased remineralization of organic matter in the upper and intermediate ocean layers that would develop in a scenario of increased stratification.

According to the obtained pH projections in Fig. 4, the pH of surface waters in the Iceland basin could drop ~ 0.35 units with respect to the pre-industrial era by the time atmospheric CO_2 reaches 800 ppm, which is consistent with outputs from coupled climate/carbon-cycle models (Caldeira and Wickett, 2005; Orr et al., 2005). In the case of *c*LSW, the linear projection predicts a pH decrease of more than 0.45 units with respect to pre-industrial pH values by the time atmospheric $x\text{CO}_2$ reaches ~ 775 ppm (about twice the present atmospheric CO_2 concentration). This result is 0.25 pH units lower than the values predicted by the well-known climate-carbon coupled model in Caldeira and Wickett (2003) for the same $x\text{CO}_2$ and ocean region. The difference between our observation-based prediction and the latter model (Caldeira and Wickett, 2003) could be due to

the fact that our data is largely extrapolated and also that it is still difficult for General Circulation Models (GCMs) to model accurately the Meridional Overturning Circulation (MOC), its NAO-related variability (Danabasoglu et al., 2012) and the deep winter convection of the NASPG. The NAO-related MOC variability has a strong influence on C_{ant} storage in the NASPG (Pérez et al., 2010) and it is therefore expected that this will affect the long-term variability of pH too, in a way models cannot quite account for yet. In this sense, our results are a good complement to model outputs. On the other hand, it has also been reported that ocean acidification might be proceeding more rapidly than models have predicted (Wootton et al., 2008), as the contemporary CO_2 emissions are actually exceeding future scenarios based on business-as-usual emission rates (Canadell et al., 2007; Raupach et al., 2007). Such reports are consistent with the lower pH predictions we obtained compared to Caldeira and Wickett (2003).

The aragonite saturation state is defined as $\Omega_{\text{arag}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K'_{\text{sp}}$, where square brackets indicate seawater ion concentrations and K'_{sp} is the apparent solubility product of aragonite (Mucci, 1983). Because $[\text{Ca}^{2+}]$ is highly and positively correlated with salinity, Ω_{arag} is largely determined by variations in $[\text{CO}_3^{2-}]$. This characteristic makes Ω_{arag} an optimum indicator for environmental availability of dissolved carbonate ions.

From the measured pH data and our pH projections (Fig. 4) we calculated the Ω_{arag} of the SPMW and *c*LSW in the Iceland basin for atmospheric $x\text{CO}_2$ values of 380 (present day), 500 and 750 ppm (see insets in Fig. 4). The results suggest that *c*LSW would actually reach aragonite undersaturation ($\Omega_{\text{arag}} < 1$) by the time atmospheric CO_2 reaches ~550 ppm and not 900 ppm, as suggested by the model predictions in Orr et al., 2005. The high-NAO enhanced ventilation that occurred towards the mid-late 1980s fostered the fast formation of a massive *c*LSW vintage (Kieke et al., 2007; Yashayaev et al., 2008). The rapid subduction of this newly formed *c*LSW injected C_{ant} from surface to intermediate waters, transporting C_{ant} much faster than via downward diffusion alone, thus causing a faster acidification rate in the *c*LSW (where organic matter remineralization

also contributes significantly to the pH lowering) than in the SPMW, where C_{ant} influence is the main contributor to acidification. Depending on the future CO_2 emission rates the 550 ppm threshold at which, according to our projections, $c\text{LSW}$ would face aragonite undersaturation, could be trespassed in 2050, or before (Nakicenovic et al., 2000; Caldeira and Wickett, 2005; Feely et al., 2009). Guinotte et al. (2006) have in fact pointed out that some deep-sea cold-water corals may experience undersaturated waters as early as 2020 under an IPCC “business-as-usual” CO_2 emission pathway, which is in good agreement with our observation-based results for the Iceland and Irminger basins.

The data analysis also showed that the aragonite saturation depth (or lysocline = isopleth where $\Omega_{\text{arag}} = 1$) has shoaled at a rate of 7 and 4 m yr^{-1} between 1981 and 2008 in the Irminger and Iceland basins, respectively. The latter is in agreement with previous local studies (Olafsson et al., 2009). The fast rate of lysocline shoaling in the Irminger basin is promoted by the intense NAO-enhanced deep convection that injects ventilated, CO_2 -rich waters into deeper layers (Messias et al., 2008), as mentioned previously. For comparison sake, the shoaling rates of the lysocline were estimated to be $\sim 0.2 \text{ m yr}^{-1}$ during the Paleocene-Eocene Thermal Maximum (55 million years ago), when a massive natural release of CO_2 into the atmosphere caused global temperatures to raise more than 5 °C in less than 10,000 years (Pelejero et al., 2010).

5. Conclusions

The progressive acidification of North Atlantic waters has been assessed from direct observations of pH spanning the last three decades. The increasing atmospheric CO_2 concentrations have largely affected the pH of surface and intermediate waters in the three studied North Atlantic regions, at varying extents. Most importantly, the LSW has shown very high acidification rates that are amongst the highest in the NASPG. In the Irminger basin, the acidification rate of $c\text{LSW}$ responds to that expected from the influence of C_{ant} , while in the Iceland basin only about 50% of

the observed pH change in the cLSW is anthropic. The SAIW has the fastest acidification rate observed ($-0.0019 \pm 0.0002 \text{ yr}^{-1}$), and 75% of this pH decrease is anthropogenic. In contrast, the C_{ant} contribution to the acidification rates in the ENACW is partially compensated by the ventilation of this water mass thus explaining the moderate acidification rates observed in the upper layers of the ENA basin (compared to the Iceland and Irminger basins). Predictions from an observation-based extrapolation of the current acidification trends and rates are in agreement with model results (Caldeira and Wickett, 2005; Orr et al., 2005) in surface layers. However, our results indicate that the intermediate waters of the North Atlantic (LSW in particular) are getting acidified more rapidly than what some models predicted.

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Table captions:

Table 1 List of selected North Atlantic cruises (Fig. 1a). Acronyms denote: P.I.= principal investigator; S= variable measured with spectrophotometric techniques; P= variable measured with potentiometric techniques; Calc= pH calculated from C_T and A_T using the thermodynamic equations of the carbon system (Dickson et al., 2007) and a set of carbon dioxide dissociation constants (Dickson and Millero, 1987). Uncert. = Analytical

uncertainties of spectrophotometric, potentiometric, and calculated pH. Adjustments from a posteriori crossover analysis are listed in $\mu\text{mol kg}^{-1}$ for C_T and A_T .

Table 2 Temporal evolution (1981-2008) of the (average \pm standard error) values of salinity, potential temperature, AOU, silicate concentrations, measured pH (pH_{SWS25}), pH basin-corrections ($\Delta\text{pH}_{\text{SWS25-BA}}$) and basin-normalized pH ($\text{pH}_{\text{SWS25-BA}} = \text{pH}_{\text{SWS25}} + \Delta\text{pH}_{\text{SWS25-BA}}$) for the water masses considered in the: a) Irminger; b) Iceland; and c) ENA basins. The WOA05 lines give the climatological data used as reference values (equation 2).

Table 3 List of coefficients obtained for equation (1) using the expression in equation (2) in each water mass and basin. Between brackets are the properties associated to each “ a_i ” coefficient and the corresponding units. All “ a_i ” coefficients have been scaled up by a factor of 10^3 , except for the salinity ones (“ a_5 ”). The “n.s.” (“not significant”) variables explained very little of the pH variability and weakened the overall MLR fit so they were therefore rejected according to a stepwise method of MLR solving.

Figure captions:

Figure 1 Fig. 1a shows the study area and selected cruises. The black straight lines delimit the Irminger, Iceland and Eastern North Atlantic (ENA) basins. Fig. 1b shows the main NASPG water masses considered for this study over the salinity distribution of the OVIDE 2004 section, which gives representative coverage of the NASPG. The vertical white lines delimit the Irminger, Iceland and ENA basins. The isopycnals (horizontal white lines; σ_θ in kg m^{-3}) are the ones listed in section 2.2 and Table 2. The water mass acronyms stand for: SAIW= Sub Arctic Intermediate Water; LSW = Labrador Sea Water; NADW = North Atlantic Deep Water; SPMW = Sub Polar Mode Water; NACW = North Atlantic Central Water; MW = Mediterranean Water. The lowercase first letters “c”, “u” and “l” denote “classical”, “upper” and “lower”, respectively.

Figure 2 Evolution of measured pH_{SWs25} distributions in the NASPG from 1991 to 2008. The transect distances (km) from the southernmost tip of Greenland towards the ENA basin are in the x-axes. The vertical white lines demarcate the transition from basin to basin (Fig. 1). The thick horizontal white lines are the isopycnals shown in Fig. 1b and listed on Table 2. Water mass acronyms are the same as in Fig. 1b. The transect represented in Fig. 2a is a composite of the A01E and OACES tracks that matches closely the OVIDE section. The two-year difference between the A01E (1991) and OACES (1993) is negligible compared with the nine-year gap between this composite section and the OVIDE 2002 cruise (Fig. 2b), as demonstrated by the continuity of the pH isopleths at the grey vertical line (merging point between the A01E and OACES tracks).

Figure 3 Trends and rates of acidification between 1981 and 2008 of the studied water masses in the Irminger basin (Fig. 3a), Iceland basin (Fig. 3b) and ENA basin (Fig. 3c). The inset boxes show acidification rates (in 10^{-3} pH units yr^{-1}) and correlation coefficients (R^2). Each of the points in the scatter plots represents the average pH of a particular water mass at the time of the measurement (cruise). Considering the ample time interval (1981-2008) these pH averages represent well the annual means. The error bars represent the error of the mean plus the uncertainty due to the basin normalization of the data (section 2.2.1).

Figure 4 Extrapolation of the observed linear trends of acidification for the SPMW and *c*LSW in the Iceland basin. On the x-axis the projections range from the pre-industrial 280 ppm to future 800 ppm of atmospheric $x\text{CO}_2$ (molar fraction of CO_2). The prediction bands give the 95% confidence intervals for the projected linear trends. The percentage aragonite

saturation states (Ω_{arag}) for present $x\text{CO}_2$ (~380 ppm) and for the horizons of 500 and 750 ppm are given in the top boxes.

Table 1.

Cruises and pH measurements								Adjustments		
Section	Year	P.I.	Expocode	#Stations	#Samples	pH	Uncert.	pH	C _T ⁽¹⁾	A _T ⁽²⁾
TTO	1981	T. Takahashi	316N19810923	30	591	Calc	0.008	0	-3.0	-3.6
BD3	1989	M. Arhan	35LU19890509	20	218	P	0.005	0.024	0	0
TYRO	1990	G. Fransz	64TR19900417	11	189	Calc	0.006	0	0	14
AR07E	1991	H.M. van Aken	64TR19910408	30	616	Calc	0.006	0	6	0
A01E	1991	J. Meincke	06MT18_1	26	431	Calc	0.006	0	0	0
OACES	1993	R. Wanninkhof	OACES93	28	497	Calc	0.006	0	0	0
FOUREX	1997	S. Bacon	74DI19970807	83	1458	S	0.002	-0.005	0	0
MET97	1997	F. Schott	06MT19970707	8	148	Calc	0.008	0	0	0
CHAOS	1998	Smythe-Wright	74DI19980423	26	459	S	0.002	0.018	0	-8.5
OVIDE'02	2002	H. Mercier	35TH20020611	85	1829	S	0.002	0	0	0
A16N	2003	J. Bullister	33RO20030604	25	693	Calc	0.006	0	0	0
OVIDE'04	2004	T. Huck	35TH20040604	98	2091	S	0.002	0	0	0
OVIDE'06	2006	P. Lherminier	06M220060523	89	1937	S	0.002	0	0	0
OVIDE'08	2008	B. Ferron	35TH20080610	87	2012	S	0.002	0	0	0

(1) C_T analysed with SOMMA (Johnson et al., 1993) and calibrated with CRMs, except in 1981 TTO cruise that was determined potentiometrically (Bradshaw et al., 1981) without CRMs. Analytical accuracy $\pm 2 \mu\text{mol}\cdot\text{kg}^{-1}$.

(2) A_T analysed with potentiometric titration and determined by developing either a full titration curve (Millero et al., 1993; Dickson et al., 2007) or from single point titration (Pérez and Fraga, 1987; Mintrop et al., 2002). Analytical accuracy $\pm 4 \mu\text{mol}\cdot\text{kg}^{-1}$.

Table 2a. Irminger Basin

Year	Salinity	θ (°C)	AOU ($\mu\text{mol}\cdot\text{kg}^{-1}$)	$\text{Si}(\text{OH})_4$ ($\mu\text{mol}\cdot\text{kg}^{-1}$)	pH_{SWS25}	$\Delta\text{pH}_{\text{SWS25-BA}}$	$\text{pH}_{\text{SWS25-BA}}$
SAIW ($\sigma_0 < 27.68 \text{ kg m}^{-3}$)							
1981	34.894 ± 0.002	5.370 ± 0.006	18.6 ± 0.3	7.96 ± 0.09	7.776 ± 0.002	0.014 ± 0.003	7.790 ± 0.003
1991	34.981 ± 0.002	5.228 ± 0.010	19.0 ± 0.5	8.50 ± 0.15	7.768 ± 0.002	0.006 ± 0.003	7.774 ± 0.004
1991	34.962 ± 0.001	5.482 ± 0.004	25.8 ± 0.2	8.96 ± 0.05	7.756 ± 0.001	0.016 ± 0.003	7.772 ± 0.003
1997	34.911 ± 0.001	5.902 ± 0.005	27.9 ± 0.2	7.69 ± 0.07	7.758 ± 0.001	0.007 ± 0.003	7.764 ± 0.003
1997	34.893 ± 0.001	5.134 ± 0.003	30.1 ± 0.2	8.83 ± 0.05	7.736 ± 0.001	0.027 ± 0.003	7.763 ± 0.003
2002	34.949 ± 0.001	5.362 ± 0.004	24.6 ± 0.2	8.08 ± 0.06	7.747 ± 0.001	0.006 ± 0.003	7.753 ± 0.003
2004	34.967 ± 0.001	5.611 ± 0.003	23.8 ± 0.1	7.93 ± 0.04	7.746 ± 0.001	0.000 ± 0.003	7.746 ± 0.003
2006	34.977 ± 0.001	5.660 ± 0.003	24.1 ± 0.1	7.88 ± 0.04	7.745 ± 0.001	-0.003 ± 0.003	7.742 ± 0.003
2008	34.978 ± 0.001	5.926 ± 0.002	12.4 ± 0.1	7.17 ± 0.04	7.757 ± 0.001	-0.013 ± 0.003	7.744 ± 0.003
WOA05	34.964 ± 0.004	5.544 ± 0.027	19.7 ± 0.3	7.89 ± 0.04	*	*	*
<i>u</i>LSW ($27.68 < \sigma_0 < 27.76 \text{ kg m}^{-3}$)							
1981	34.865 ± 0.001	3.534 ± 0.004	28.1 ± 0.2	9.28 ± 0.07	7.749 ± 0.001	0.022 ± 0.002	7.771 ± 0.002
1991	34.889 ± 0.001	3.577 ± 0.004	24.2 ± 0.2	9.52 ± 0.07	7.745 ± 0.001	0.010 ± 0.002	7.755 ± 0.002
1991	34.900 ± 0.001	3.728 ± 0.003	28.7 ± 0.2	10.05 ± 0.05	7.740 ± 0.001	0.013 ± 0.002	7.753 ± 0.002
1997	34.877 ± 0.001	3.533 ± 0.005	35.6 ± 0.3	9.67 ± 0.08	7.725 ± 0.001	0.017 ± 0.002	7.742 ± 0.002
1997	34.869 ± 0.001	3.520 ± 0.003	35.9 ± 0.1	10.17 ± 0.04	7.716 ± 0.001	0.029 ± 0.002	7.746 ± 0.002
2002	34.896 ± 0.001	3.803 ± 0.003	35.0 ± 0.1	9.30 ± 0.04	7.725 ± 0.001	0.010 ± 0.002	7.735 ± 0.002
2004	34.888 ± 0.001	3.710 ± 0.003	37.2 ± 0.1	9.50 ± 0.04	7.719 ± 0.001	0.014 ± 0.002	7.733 ± 0.002
2006	34.902 ± 0.001	3.831 ± 0.002	34.4 ± 0.1	9.48 ± 0.04	7.720 ± 0.001	0.008 ± 0.002	7.728 ± 0.002
2008	34.908 ± 0.001	3.913 ± 0.002	27.2 ± 0.1	9.21 ± 0.03	7.721 ± 0.001	0.004 ± 0.002	7.725 ± 0.002
WOA05	34.925 ± 0.002	3.997 ± 0.020	33.5 ± 0.2	9.62 ± 0.04	*	*	*
<i>c</i>LSW ($27.6 < \sigma_0 < 27.81 \text{ kg m}^{-3}$)							
1981	34.917 ± 0.002	3.375 ± 0.008	39.1 ± 0.4	10.58 ± 0.12	7.749 ± 0.002	0.008 ± 0.002	7.757 ± 0.003
1991	34.879 ± 0.001	3.137 ± 0.003	32.6 ± 0.2	10.16 ± 0.05	7.742 ± 0.001	0.007 ± 0.002	7.749 ± 0.002
1991	34.881 ± 0.001	3.156 ± 0.003	29.8 ± 0.1	10.30 ± 0.04	7.738 ± 0.001	0.009 ± 0.002	7.747 ± 0.002
1997	34.871 ± 0.001	2.986 ± 0.004	31.1 ± 0.2	9.94 ± 0.06	7.729 ± 0.001	0.015 ± 0.002	7.744 ± 0.002
1997	34.868 ± 0.001	2.989 ± 0.003	30.9 ± 0.1	10.43 ± 0.04	7.722 ± 0.001	0.022 ± 0.002	7.743 ± 0.002
2002	34.897 ± 0.001	3.184 ± 0.003	38.8 ± 0.2	10.23 ± 0.05	7.727 ± 0.001	0.011 ± 0.002	7.738 ± 0.002
2004	34.902 ± 0.001	3.232 ± 0.004	40.5 ± 0.2	10.44 ± 0.06	7.722 ± 0.001	0.013 ± 0.002	7.735 ± 0.002
2006	34.923 ± 0.001	3.369 ± 0.003	40.8 ± 0.2	10.58 ± 0.05	7.723 ± 0.001	0.011 ± 0.002	7.734 ± 0.002
2008	34.924 ± 0.001	3.383 ± 0.003	39.5 ± 0.2	10.72 ± 0.05	7.722 ± 0.001	0.013 ± 0.002	7.734 ± 0.002
WOA05	34.899 ± 0.001	3.314 ± 0.012	35.7 ± 0.1	10.25 ± 0.03	*	*	*
<i>u</i>NADW ($27.81 < \sigma_0 < 27.88 \text{ kg m}^{-3}$)							
1981	34.948 ± 0.001	2.980 ± 0.005	44.3 ± 0.2	12.01 ± 0.07	7.750 ± 0.001	0.000 ± 0.003	7.750 ± 0.003
1991	34.940 ± 0.001	2.925 ± 0.003	48.4 ± 0.2	12.66 ± 0.05	7.745 ± 0.001	0.000 ± 0.003	7.745 ± 0.003
1991	34.935 ± 0.001	2.887 ± 0.003	44.9 ± 0.2	12.79 ± 0.05	7.745 ± 0.001	0.000 ± 0.003	7.745 ± 0.003
1997	34.917 ± 0.001	2.785 ± 0.005	41.5 ± 0.3	11.26 ± 0.08	7.740 ± 0.001	0.000 ± 0.003	7.740 ± 0.003
1997	34.924 ± 0.001	2.813 ± 0.004	44.2 ± 0.2	12.81 ± 0.06	7.733 ± 0.001	0.000 ± 0.003	7.733 ± 0.003
2002	34.918 ± 0.001	2.759 ± 0.003	43.7 ± 0.1	11.50 ± 0.04	7.732 ± 0.001	0.000 ± 0.003	7.732 ± 0.003
2004	34.916 ± 0.001	2.753 ± 0.003	44.4 ± 0.1	11.70 ± 0.04	7.726 ± 0.001	0.000 ± 0.003	7.726 ± 0.003
2006	34.930 ± 0.001	2.859 ± 0.003	43.2 ± 0.1	11.70 ± 0.04	7.728 ± 0.001	0.000 ± 0.003	7.728 ± 0.003
2008	34.931 ± 0.001	2.872 ± 0.003	41.4 ± 0.2	11.96 ± 0.05	7.726 ± 0.001	0.000 ± 0.003	7.726 ± 0.003
WOA05	34.915 ± 0.003	2.869 ± 0.028	42.7 ± 0.2	11.30 ± 0.10	*	*	*
DSOW ($\sigma_0 > 27.88 \text{ kg m}^{-3}$)							
1981	34.892 ± 0.002	1.679 ± 0.008	36.7 ± 0.4	9.80 ± 0.12	7.749 ± 0.002	0.000 ± 0.005	7.749 ± 0.006
1991	34.897 ± 0.001	1.778 ± 0.005	41.6 ± 0.3	10.20 ± 0.08	7.742 ± 0.001	0.000 ± 0.005	7.742 ± 0.005
1991	34.896 ± 0.001	1.794 ± 0.006	38.1 ± 0.3	10.57 ± 0.09	7.742 ± 0.001	0.000 ± 0.005	7.742 ± 0.005
1997	34.897 ± 0.002	1.772 ± 0.009	38.0 ± 0.5	9.73 ± 0.14	7.726 ± 0.002	0.000 ± 0.005	7.726 ± 0.006
1997	34.894 ± 0.002	1.720 ± 0.008	38.8 ± 0.4	11.11 ± 0.13	7.724 ± 0.002	0.000 ± 0.005	7.724 ± 0.006
2002	34.887 ± 0.001	1.721 ± 0.005	39.4 ± 0.3	9.53 ± 0.08	7.731 ± 0.001	0.000 ± 0.005	7.731 ± 0.005
2004	34.869 ± 0.001	1.535 ± 0.005	36.3 ± 0.2	8.92 ± 0.07	7.723 ± 0.001	0.000 ± 0.005	7.723 ± 0.005
2006	34.906 ± 0.001	1.874 ± 0.004	37.7 ± 0.2	9.77 ± 0.07	7.726 ± 0.001	0.000 ± 0.005	7.726 ± 0.005
2008	34.908 ± 0.001	1.797 ± 0.006	36.4 ± 0.3	10.06 ± 0.09	7.721 ± 0.001	0.000 ± 0.005	7.721 ± 0.005
WOA05	34.895 ± 0.004	1.885 ± 0.064	40.1 ± 0.2	11.08 ± 0.19	*	*	*

Table 2b. Iceland Basin

Year	Salinity	θ (°C)	AOU ($\mu\text{mol}\cdot\text{kg}^{-1}$)	$\text{Si}(\text{OH})_4$ ($\mu\text{mol}\cdot\text{kg}^{-1}$)	pH_{SWS25}	$\Delta\text{pH}_{\text{SWS25-BA}}$	$\text{pH}_{\text{SWS25-BA}}$
SPMW ($\sigma_0 < 27.60 \text{ kg m}^{-3}$)							
1981	35.183 ± 0.001	8.242 ± 0.003	28.2 ± 0.1	6.89 ± 0.04	7.814 ± 0.001	-0.008 ± 0.005	7.806 ± 0.005
1991	35.109 ± 0.001	7.030 ± 0.003	22.9 ± 0.2	7.73 ± 0.05	7.797 ± 0.001	0.005 ± 0.005	7.802 ± 0.005
1991	35.000 ± 0.002	6.935 ± 0.007	37.8 ± 0.3	8.94 ± 0.10	7.757 ± 0.001	0.030 ± 0.005	7.787 ± 0.005
1993	35.151 ± 0.001	7.889 ± 0.003	31.6 ± 0.1	6.68 ± 0.04	7.789 ± 0.001	0.004 ± 0.005	7.793 ± 0.005
1997	35.094 ± 0.001	7.931 ± 0.003	47.2 ± 0.2	8.17 ± 0.05	7.769 ± 0.001	0.028 ± 0.005	7.797 ± 0.005
1998	35.249 ± 0.001	8.563 ± 0.003	28.7 ± 0.2	7.22 ± 0.05	7.796 ± 0.001	-0.011 ± 0.005	7.785 ± 0.005
2002	35.117 ± 0.001	7.614 ± 0.003	30.5 ± 0.2	7.33 ± 0.05	7.776 ± 0.001	0.008 ± 0.005	7.784 ± 0.005
2003	35.260 ± 0.001	8.826 ± 0.002	37.4 ± 0.1	6.68 ± 0.03	7.785 ± 0.001	-0.002 ± 0.005	7.783 ± 0.005
2004	35.105 ± 0.001	7.719 ± 0.002	38.5 ± 0.1	7.40 ± 0.04	7.763 ± 0.001	0.018 ± 0.005	7.782 ± 0.005
2006	35.077 ± 0.001	7.906 ± 0.003	38.7 ± 0.1	7.20 ± 0.04	7.765 ± 0.001	0.016 ± 0.005	7.781 ± 0.005
2008	35.111 ± 0.001	7.809 ± 0.002	28.1 ± 0.1	6.84 ± 0.04	7.771 ± 0.001	0.000 ± 0.005	7.771 ± 0.005
WOA05	35.175 ± 0.002	7.954 ± 0.027	29.6 ± 0.4	7.36 ± 0.04	*	*	*
<i>u</i>LSW ($\sigma_0 > 27.60 \text{ kg m}^{-3}$; $\sigma_1 < 32.35 \text{ kg m}^{-3}$)							
1981	34.982 ± 0.001	4.637 ± 0.005	48.5 ± 0.3	10.56 ± 0.08	7.739 ± 0.001	-0.002 ± 0.002	7.737 ± 0.002
1991	34.959 ± 0.001	4.488 ± 0.004	56.2 ± 0.2	10.87 ± 0.06	7.726 ± 0.001	0.000 ± 0.002	7.727 ± 0.002
1991	34.944 ± 0.001	4.340 ± 0.006	51.7 ± 0.3	11.16 ± 0.09	7.728 ± 0.001	0.002 ± 0.002	7.729 ± 0.002
1993	34.987 ± 0.001	4.754 ± 0.004	56.0 ± 0.2	10.43 ± 0.06	7.730 ± 0.001	-0.003 ± 0.002	7.727 ± 0.002
1997	34.940 ± 0.001	4.345 ± 0.003	55.7 ± 0.2	11.11 ± 0.05	7.715 ± 0.001	0.002 ± 0.002	7.717 ± 0.002
1998	35.009 ± 0.002	4.938 ± 0.007	62.2 ± 0.3	11.72 ± 0.10	7.712 ± 0.001	0.006 ± 0.002	7.718 ± 0.002
2002	34.976 ± 0.001	4.657 ± 0.003	57.5 ± 0.2	10.60 ± 0.05	7.716 ± 0.001	-0.002 ± 0.002	7.714 ± 0.002
2003	35.024 ± 0.001	4.979 ± 0.004	63.7 ± 0.2	11.24 ± 0.06	7.709 ± 0.001	0.003 ± 0.002	7.712 ± 0.002
2004	34.948 ± 0.001	4.408 ± 0.002	55.7 ± 0.1	10.68 ± 0.04	7.709 ± 0.001	0.000 ± 0.002	7.708 ± 0.002
2006	34.956 ± 0.001	4.494 ± 0.003	54.4 ± 0.1	10.74 ± 0.04	7.707 ± 0.001	-0.001 ± 0.002	7.706 ± 0.002
2008	34.952 ± 0.001	4.451 ± 0.003	51.1 ± 0.1	10.50 ± 0.04	7.709 ± 0.001	-0.002 ± 0.002	7.707 ± 0.002
WOA05	35.015 ± 0.002	4.924 ± 0.001	54.1 ± 0.3	10.79 ± 0.05	*	*	*
<i>c</i>LSW ($\sigma_1 > 32.35 \text{ kg m}^{-3}$; $\sigma_2 < 37.00 \text{ kg m}^{-3}$)							
1981	34.943 ± 0.001	3.517 ± 0.004	44.7 ± 0.2	12.13 ± 0.07	7.738 ± 0.001	0.009 ± 0.006	7.747 ± 0.006
1991	34.928 ± 0.001	3.376 ± 0.003	45.6 ± 0.1	11.59 ± 0.04	7.746 ± 0.001	-0.002 ± 0.006	7.743 ± 0.006
1991	34.923 ± 0.001	3.308 ± 0.005	43.5 ± 0.3	12.31 ± 0.08	7.740 ± 0.001	0.002 ± 0.006	7.742 ± 0.006
1993	34.926 ± 0.001	3.458 ± 0.005	44.6 ± 0.2	11.27 ± 0.07	7.737 ± 0.001	-0.003 ± 0.006	7.735 ± 0.006
1997	34.905 ± 0.001	3.170 ± 0.002	40.1 ± 0.1	11.72 ± 0.04	7.732 ± 0.001	-0.009 ± 0.006	7.723 ± 0.006
1998	34.919 ± 0.002	3.372 ± 0.006	44.1 ± 0.3	12.08 ± 0.09	7.718 ± 0.001	0.003 ± 0.006	7.721 ± 0.006
2002	34.920 ± 0.001	3.273 ± 0.003	43.1 ± 0.1	11.06 ± 0.04	7.727 ± 0.001	-0.013 ± 0.006	7.714 ± 0.006
2003	34.926 ± 0.001	3.387 ± 0.005	45.2 ± 0.3	11.79 ± 0.08	7.714 ± 0.001	0.000 ± 0.006	7.714 ± 0.006
2004	34.909 ± 0.001	3.226 ± 0.003	43.8 ± 0.1	11.32 ± 0.04	7.722 ± 0.001	-0.011 ± 0.006	7.711 ± 0.006
2006	34.919 ± 0.001	3.297 ± 0.003	42.2 ± 0.1	11.39 ± 0.04	7.722 ± 0.001	-0.008 ± 0.006	7.714 ± 0.006
2008	34.923 ± 0.001	3.299 ± 0.003	42.6 ± 0.1	11.50 ± 0.04	7.722 ± 0.001	-0.006 ± 0.006	7.716 ± 0.006
WOA05	34.936 ± 0.001	3.414 ± 0.012	45.1 ± 0.1	11.67 ± 0.05	*	*	*
<i>u</i>NADW ($\sigma_2 > 37.00 \text{ kg m}^{-3}$; $\sigma_4 < 45.84 \text{ kg m}^{-3}$)							
1981	34.970 ± 0.002	2.732 ± 0.007	52.9 ± 0.3	10.74 ± 0.10	7.739 ± 0.001	0.007 ± 0.006	7.746 ± 0.007
1991	34.972 ± 0.001	2.762 ± 0.004	53.0 ± 0.2	14.66 ± 0.05	7.739 ± 0.001	0.006 ± 0.006	7.745 ± 0.007
1991	34.963 ± 0.001	2.718 ± 0.005	55.2 ± 0.2	18.44 ± 0.07	7.739 ± 0.001	0.000 ± 0.006	7.739 ± 0.007
1993	34.971 ± 0.003	2.816 ± 0.012	49.3 ± 0.6	12.95 ± 0.18	7.741 ± 0.001	0.006 ± 0.006	7.747 ± 0.007
1997	34.949 ± 0.001	2.689 ± 0.004	50.0 ± 0.2	15.53 ± 0.06	7.733 ± 0.001	0.003 ± 0.006	7.736 ± 0.007
1998	34.967 ± 0.004	2.749 ± 0.017	49.7 ± 0.9	13.69 ± 0.26	7.721 ± 0.002	0.010 ± 0.006	7.731 ± 0.007
2002	34.964 ± 0.001	2.704 ± 0.004	52.8 ± 0.2	15.52 ± 0.05	7.727 ± 0.001	0.007 ± 0.006	7.734 ± 0.007
2003	34.975 ± 0.003	2.833 ± 0.012	48.3 ± 0.6	13.51 ± 0.18	7.715 ± 0.001	0.007 ± 0.006	7.722 ± 0.007
2004	34.959 ± 0.001	2.675 ± 0.004	56.0 ± 0.2	17.09 ± 0.06	7.724 ± 0.001	0.002 ± 0.006	7.726 ± 0.007
2006	34.964 ± 0.001	2.705 ± 0.003	53.2 ± 0.2	17.54 ± 0.05	7.724 ± 0.001	0.007 ± 0.006	7.731 ± 0.007
2008	34.964 ± 0.001	2.701 ± 0.004	52.3 ± 0.2	16.37 ± 0.06	7.722 ± 0.001	0.010 ± 0.006	7.731 ± 0.007
WOA05	34.963 ± 0.004	2.710 ± 0.025	56.5 ± 0.3	18.77 ± 0.77	*	*	*

Table 2c. ENA Basin

Year	Salinity	θ (°C)	AOU ($\mu\text{mol}\cdot\text{kg}^{-1}$)	$\text{Si}(\text{OH})_4$ ($\mu\text{mol}\cdot\text{kg}^{-1}$)	pH _{SWS25}	$\Delta\text{pH}_{\text{SWS25-BA}}$	pH _{SWS25-BA}
NACW ($\sigma_0 < 27.20 \text{ kg m}^{-3}$)							
1981	35.618 ± 0.001	12.472 ± 0.003	27.5 ± 0.2	3.74 ± 0.05	7.883 ± 0.001	0.004 ± 0.004	7.887 ± 0.004
1989	35.661 ± 0.001	12.448 ± 0.004	23.6 ± 0.2	2.86 ± 0.06	7.871 ± 0.001	-0.001 ± 0.004	7.871 ± 0.004
1990	35.668 ± 0.001	12.160 ± 0.003	19.7 ± 0.1	3.52 ± 0.04	7.874 ± 0.001	0.001 ± 0.004	7.875 ± 0.004
1991	35.532 ± 0.004	11.163 ± 0.015	22.5 ± 0.8	4.66 ± 0.23	7.860 ± 0.002	0.013 ± 0.004	7.873 ± 0.004
1993	35.544 ± 0.001	11.500 ± 0.004	23.0 ± 0.2	3.02 ± 0.07	7.866 ± 0.001	0.010 ± 0.004	7.876 ± 0.004
1997	35.673 ± 0.000	12.375 ± 0.002	31.6 ± 0.1	3.58 ± 0.03	7.861 ± 0.001	0.010 ± 0.004	7.871 ± 0.004
1998	35.659 ± 0.001	12.293 ± 0.002	20.9 ± 0.1	3.62 ± 0.03	7.876 ± 0.001	-0.001 ± 0.004	7.874 ± 0.004
2002	35.643 ± 0.000	12.170 ± 0.002	26.1 ± 0.1	3.58 ± 0.03	7.860 ± 0.001	0.006 ± 0.004	7.866 ± 0.004
2003	35.657 ± 0.000	12.492 ± 0.002	25.1 ± 0.1	3.47 ± 0.03	7.862 ± 0.001	0.001 ± 0.004	7.863 ± 0.004
2004	35.637 ± 0.000	12.116 ± 0.002	28.5 ± 0.1	3.63 ± 0.03	7.854 ± 0.001	0.009 ± 0.004	7.864 ± 0.004
2006	35.659 ± 0.000	12.146 ± 0.002	24.1 ± 0.1	3.43 ± 0.03	7.853 ± 0.001	0.004 ± 0.004	7.857 ± 0.004
2008	35.673 ± 0.000	12.562 ± 0.002	24.1 ± 0.1	3.45 ± 0.02	7.861 ± 0.001	-0.002 ± 0.004	7.859 ± 0.004
WOA05	35.552 ± 0.004	11.832 ± 0.029	17.9 ± 0.3	3.47 ± 0.02	*	*	*
MW ($\sigma_0 > 27.20 \text{ kg m}^{-3}$; $\sigma_1 < 32.35 \text{ kg m}^{-3}$)							
1981	35.408 ± 0.001	7.812 ± 0.003	72.4 ± 0.1	10.29 ± 0.04	7.761 ± 0.001	0.019 ± 0.002	7.780 ± 0.002
1989	35.745 ± 0.001	9.679 ± 0.003	74.4 ± 0.2	9.34 ± 0.05	7.781 ± 0.001	-0.009 ± 0.002	7.772 ± 0.002
1990	35.250 ± 0.001	7.156 ± 0.004	64.2 ± 0.2	10.07 ± 0.05	7.749 ± 0.001	0.019 ± 0.002	7.767 ± 0.002
1991	35.107 ± 0.001	6.650 ± 0.003	54.1 ± 0.2	10.07 ± 0.05	7.756 ± 0.001	0.015 ± 0.002	7.772 ± 0.002
1993	35.242 ± 0.001	7.125 ± 0.003	64.9 ± 0.1	9.08 ± 0.04	7.754 ± 0.001	0.019 ± 0.002	7.774 ± 0.002
1997	35.509 ± 0.000	8.413 ± 0.002	75.4 ± 0.1	9.77 ± 0.02	7.759 ± 0.001	0.010 ± 0.002	7.770 ± 0.002
1998	35.323 ± 0.001	7.542 ± 0.003	74.6 ± 0.2	10.46 ± 0.05	7.744 ± 0.001	0.023 ± 0.002	7.767 ± 0.002
2002	35.490 ± 0.000	8.262 ± 0.001	74.2 ± 0.1	9.66 ± 0.02	7.756 ± 0.001	0.011 ± 0.002	7.767 ± 0.002
2003	35.365 ± 0.001	7.771 ± 0.002	78.5 ± 0.1	10.21 ± 0.03	7.743 ± 0.001	0.023 ± 0.002	7.766 ± 0.002
2004	35.456 ± 0.000	8.038 ± 0.001	75.2 ± 0.1	9.86 ± 0.02	7.751 ± 0.001	0.015 ± 0.002	7.766 ± 0.002
2006	35.493 ± 0.000	8.218 ± 0.001	75.1 ± 0.1	9.76 ± 0.02	7.749 ± 0.001	0.012 ± 0.002	7.761 ± 0.002
2008	35.445 ± 0.000	7.998 ± 0.001	70.6 ± 0.1	9.69 ± 0.02	7.751 ± 0.001	0.010 ± 0.002	7.761 ± 0.002
WOA05	35.395 ± 0.004	8.176 ± 0.037	60.2 ± 0.7	9.28 ± 0.05	*	*	*
LSW ($\sigma_1 > 32.35 \text{ kg m}^{-3}$; $\sigma_2 < 37.00 \text{ kg m}^{-3}$)							
1981	35.057 ± 0.001	3.975 ± 0.004	56.0 ± 0.2	15.15 ± 0.06	7.746 ± 0.001	0.003 ± 0.004	7.749 ± 0.004
1989	35.107 ± 0.001	4.353 ± 0.006	62.7 ± 0.3	16.90 ± 0.09	7.734 ± 0.001	0.004 ± 0.004	7.737 ± 0.004
1990	35.002 ± 0.002	3.712 ± 0.006	54.5 ± 0.3	14.41 ± 0.10	7.734 ± 0.001	0.013 ± 0.004	7.747 ± 0.004
1991	34.920 ± 0.001	3.286 ± 0.004	45.4 ± 0.2	13.21 ± 0.06	7.743 ± 0.001	-0.003 ± 0.004	7.739 ± 0.004
1993	34.946 ± 0.001	3.422 ± 0.004	47.2 ± 0.2	12.33 ± 0.05	7.743 ± 0.001	-0.002 ± 0.004	7.740 ± 0.004
1997	34.997 ± 0.001	3.673 ± 0.002	55.0 ± 0.1	15.27 ± 0.03	7.734 ± 0.001	0.007 ± 0.004	7.740 ± 0.004
1998	34.962 ± 0.001	3.515 ± 0.004	50.2 ± 0.2	13.94 ± 0.05	7.730 ± 0.001	0.003 ± 0.004	7.733 ± 0.004
2002	34.990 ± 0.001	3.636 ± 0.002	51.9 ± 0.1	14.01 ± 0.03	7.732 ± 0.001	-0.004 ± 0.004	7.729 ± 0.004
2003	34.957 ± 0.001	3.466 ± 0.003	52.6 ± 0.2	13.60 ± 0.05	7.734 ± 0.001	-0.004 ± 0.004	7.730 ± 0.004
2004	34.986 ± 0.000	3.606 ± 0.002	53.0 ± 0.1	14.01 ± 0.02	7.730 ± 0.001	0.003 ± 0.004	7.732 ± 0.004
2006	34.989 ± 0.000	3.642 ± 0.002	50.7 ± 0.1	13.54 ± 0.03	7.729 ± 0.001	-0.001 ± 0.004	7.728 ± 0.004
2008	34.994 ± 0.000	3.657 ± 0.002	51.8 ± 0.1	14.00 ± 0.03	7.731 ± 0.001	-0.005 ± 0.004	7.727 ± 0.004
WOA05	34.990 ± 0.005	3.673 ± 0.031	55.4 ± 0.4	14.99 ± 0.13	*	*	*
uNADW ($\sigma_2 > 37.00 \text{ kg m}^{-3}$; $\sigma_4 < 45.84 \text{ kg m}^{-3}$)							
1981	34.947 ± 0.001	2.610 ± 0.005	71.7 ± 0.2	30.40 ± 0.07	7.738 ± 0.001	-0.011 ± 0.003	7.727 ± 0.003
1989	34.959 ± 0.001	2.738 ± 0.005	74.7 ± 0.3	31.98 ± 0.08	7.726 ± 0.001	-0.009 ± 0.003	7.718 ± 0.003
1990	34.947 ± 0.002	2.571 ± 0.009	75.9 ± 0.5	32.14 ± 0.14	7.710 ± 0.001	0.008 ± 0.003	7.718 ± 0.003
1991	34.943 ± 0.001	2.574 ± 0.004	68.5 ± 0.2	28.34 ± 0.06	7.738 ± 0.001	-0.020 ± 0.003	7.718 ± 0.003
1993	34.945 ± 0.001	2.585 ± 0.006	69.4 ± 0.3	28.53 ± 0.08	7.740 ± 0.001	-0.017 ± 0.003	7.724 ± 0.003
1997	34.944 ± 0.001	2.597 ± 0.003	76.3 ± 0.1	32.62 ± 0.04	7.733 ± 0.001	-0.006 ± 0.003	7.727 ± 0.003
1998	34.941 ± 0.001	2.564 ± 0.005	72.6 ± 0.2	31.22 ± 0.07	7.731 ± 0.001	-0.012 ± 0.003	7.719 ± 0.003
2002	34.948 ± 0.000	2.611 ± 0.002	71.9 ± 0.1	30.97 ± 0.03	7.733 ± 0.001	-0.014 ± 0.003	7.719 ± 0.003
2003	34.938 ± 0.001	2.515 ± 0.005	77.3 ± 0.2	31.52 ± 0.07	7.720 ± 0.001	-0.001 ± 0.003	7.719 ± 0.003
2004	34.943 ± 0.000	2.588 ± 0.002	73.8 ± 0.1	31.17 ± 0.03	7.732 ± 0.001	-0.012 ± 0.003	7.719 ± 0.003
2006	34.950 ± 0.000	2.626 ± 0.002	70.5 ± 0.1	30.81 ± 0.03	7.732 ± 0.001	-0.016 ± 0.003	7.716 ± 0.003
2008	34.945 ± 0.000	2.597 ± 0.002	72.0 ± 0.1	31.78 ± 0.03	7.734 ± 0.001	-0.018 ± 0.003	7.716 ± 0.003
WOA05	34.944 ± 0.001	2.589 ± 0.013	77.9 ± 0.2	33.02 ± 0.32	*	*	*
lNADW ($\sigma_4 > 45.84 \text{ kg m}^{-3}$)							
1981	34.907 ± 0.001	2.151 ± 0.006	85.2 ± 0.3	43.67 ± 0.09	7.728 ± 0.001	-0.001 ± 0.004	7.726 ± 0.004
1989	34.905 ± 0.001	2.130 ± 0.005	85.2 ± 0.3	44.98 ± 0.08	7.719 ± 0.001	0.000 ± 0.004	7.719 ± 0.004

Table 3.

Water Mass	R ²	Estimated error	a_1 (xCO ₂ ; ppm ⁻¹)	a_2 (Si(OH) ₄ ; kg·μmol ⁻¹)	a_3 (AOU ; kg·μmol ⁻¹)	a_4 (θ ; °C ⁻¹)	a_5 (S)
Irminger Basin							
SAIW	0.97	0.003	-1.02 ± 0.08	-15 ± 2	n.s.	n.s.	0.18 ± 0.03
<i>u</i> LSW	0.99	0.002	-0.95 ± 0.04	-11 ± 1	n.s.	30 ± 10	0.67 ± 0.08
<i>c</i> LSW	0.99	0.002	-0.50 ± 0.04	-17 ± 3	n.s.	97 ± 16	0.44 ± 0.14
<i>u</i> NADW	0.89	0.003	-0.56 ± 0.07	n.s.	n.s.	n.s.	n.s.
DSOW	0.78	0.005	-0.57 ± 0.12	n.s.	n.s.	n.s.	n.s.
Iceland Basin							
SPMW	0.94	0.005	-0.61 ± 0.15	n.s.	-1.5 ± 0.3	17 ± 3	n.s.
<i>u</i> LSW	0.96	0.002	-0.72 ± 0.06	-7 ± 2	n.s.	n.s.	n.s.
<i>c</i> LSW	0.81	0.006	-0.95 ± 0.21	-11 ± 6	n.s.	-40 ± 24	n.s.
<i>u</i> NADW	0.75	0.006	-0.53 ± 0.16	n.s.	2 ± 1	n.s.	-0.8 ± 0.4
Eastern North Atlantic Basin							
NACW	0.89	0.004	-0.54 ± 0.09	n.s.	-1.2 ± 0.4	11 ± 3	n.s.
MW	0.96	0.002	-0.26 ± 0.07	n.s.	-1.0 ± 0.2	15 ± 2	n.s.
LSW	0.77	0.004	-0.42 ± 0.08	n.s.	-0.6 ± 0.2	n.s.	n.s.
<i>u</i> NADW	0.78	0.003	n.s.	n.s.	-2.3 ± 0.6	27 ± 11	-3 ± 1
<i>l</i> NADW	0.28	0.004	0.13 ± 0.10	n.s.	n.s.	20 ± 13	n.s.







