REVIEWER #2

Interactive comment on "Observed trends of anthropogenic acidification in North Atlantic water masses" by M. Vázquez-Rodríguez et al.

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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 ($\Delta pH_{SWS25\text{-}BA}$) 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 ($\Delta pH_{SWS25\text{-}BA}$); and c) basin-normalized pH averages ($pH_{SWS25\text{-}BA}$), after the expression in equation 1 ($pH_{SWS25\text{-}BA} = pH_{SWS25} + \Delta pH_{SWS25\text{-}BA}$). 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

In this paper the authors use a large collection of data for the subpolar North Atlantic (SPNA) in order to quantify the change in interior ocean pH over about 3 decades. The SPNA is well suited for this as large amounts of anthropogenic carbon (Cant) is taken up and stored in this region, and this region is relatively well sampled in comparison to other ocean regions. The SPNA is also a very active area with significant changes in water mass composition and properties over the last decades and the observational record (probably for much longer than that, but without observations to verify this). The authors show trends of observed pH trends in the SPNA over 3 decades, and attempt to project these trends linearly into the next 50 or so years. Rather than into the next 50 years, over higher atmospheric xCO_2 values (that is what was on the x-axis of Fig. S1 –now Fig. 4). Motivated by this type of confusion, we have deleted the references to the two CO_2 emission scenarios we mentioned to avoid complicating the main message. Our projections are based on xCO_2 values, not on time, or on how fast those xCO_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. The theme of the manuscript is well suited for publication in BG, but both the methods and the result/discussion sections is in the need of significant improvements. You will find that those sections have changed significantly in the revised version of the manuscript (see general comments above). They are more concise and clearer thanks to your comments and suggestions

Main concerns:

The methods section of this manuscript needs considerable improvements. **GENERAL COMMENT ON THIS SECTION:** This whole section (now 2.2.1) has been restructured and rewritten aiming for clarity and conciseness. I do not understand why the authors only use density layers that vary between basins to determine water masses. The authors have access to several other parameters that can help distinguish different water masses with similar densities. One of the reasons to select those water masses and density layers was to be able to use the results obtained in Pérez et al. 2010. The C_{ant} storage rates provided by Pérez et al. 2010 have been used to calculate the expected acidification rates due to human activities and we compared these expected rates with our observation-based results, where no separation between the anthropogenic and natural acidification signals has been done (see the second paragraph in Section 4, "Discussion"). This way, it is possible to evaluate how much of the observed acidification in the different water masses is human-induced and how much is due to natural variability. This can potentially lead to problems with some water masses such as Mediterranean Water. For the particular case of MW, we used the recommendations in Ríos et al. 1992 to select the isopycnal limits. A more serious problem is probably the temporal variability aspect of this problem. Changes in water mass properties in the SPNA are well documented, and the authors refer to some of these studies. By following isopycnals from year to year (they are the same in all panels in Fig. 2 or in new Table 2) and not average properties of the water masses (which do change indeed, as reflected by the values on new Table 2 –former supplementary tables) we minimise the risk of misplacing a given water mass. The authors write: "The main factors that modulate the natural variability of ocean pH on decadal timescales need to be removed from observations in order to isolate and evaluate the anthropogenic forcing and its effects in ocean acidification", and then sets out to remove the "natural variability". It is not clear to me why one should take out decadal variability for a study concerned with decadal changes; it seems to defeat the purpose of the study. Please, see point 1) in the general comments on the first page of this letter. This was understood wrongly in the previous version, probably because we did not express well enough what was intended. The methodology 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 to avoid sampling biases due to either the time or position of sampling with respect to the basin averages. Thanks a lot for this comment. Section 2.2.2 (now 2.2.1) was indeed the hardest part to follow in the manuscript and it has changed substantially motivated by your comments and from the rest of the reviewers. It is also not clear that the variability they apparently remove is natural. The authors present no evidence for that. If the variability is a result of anthropogenic changes effecting circulation, temperature, oxygen etc. would it not be a very bad idea to remove that signal? The section describing the normalization and averaging of pH data is very difficult to understand. Idem as in the above comment. I have tried hard, and I think I know what the authors did, but it is not clear to me why they did it this particular way; or why they did it at all, for that matter. It occurs to me as a strange way of normalizing the pH values. We believe this has improved significantly on the revised version. New section 2.2.1 has been restructured and rewritten aiming for clarity and conciseness. Please, refer to that section and to the answers to related comments in this letter.It is not clear to me that the factors (a) in equation 1 and 2 can be directly compared as the authors do, since equation 2 has one more term. The a_i coefficients obtained from new equation (3) (former equation (2) on the original version of the manuscript) are the ones needed in equation (2) to obtain $\Delta pH_{SWS25\text{-}BA}$. As a matter of fact, that is the only purpose of equation (3), i.e., obtaining the a_i coefficients from equation (2). NB: All equation numbers refer to the equations in the revised version of the manuscript (which are the same as in the previous version. They have only been reorganised). The authors state that the Delta-pHc term is spatially and seasonally detrended. We apologize for the misunderstanding and poor explanation of the methodology. We thought it was straightforward to follow, but it turned it wasn't so, so thank you for all this feedback. There's no seasonal detrending. Please, refer to new section 2.2.1. Firstly, is this not a normalization to climatological conditions for a water mass, rather than a spatial normalization? Secondly, how does the seasonal signal transports to the interior ocean? Is this even worth doing, except for the surface waters? Also, coming back to my previous concerns, why "reference to average climatological conditions" at all? The first sentence in new section 2.2.1 states exactly this: "…*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 basis of this averaging methodology has been fully described in the works by Pérez et al. (2008; 2010) and Ríos et al. 2012, to which we make a reference now to simplify this section and explain only the specifics to our case (pH) compared to theirs (the were dealing with C_{ant} instead).

Looking at the values in tables S1 to S3 there seems to be a clear decreasing trend for most water masses without any normalization to climatological conditions. Why not report on the trend of the averaged observed pH for each water mass? I think that is the very least that should be done in order for the reader to understand how large influence the "normalization" process has on the trends. The DeltapHc term is not reported on in any of the tables, which I think it should be (if at all used). Please, se point 3) to the general comments on the first page of this letter and new Table 2 (former supplementary tables). On Table 2 we give a full list of the values of a) direct measurements (pH_{SWS25}); b) basin-and-layer normalization (correction) element ($\Delta pH_{SWS25\text{-}BA}$); and c) basin-normalized pH averages ($pH_{SWS25\text{-}BA}$), after the expression in equation 1 ($pH_{SWS25\text{-}BA} = pH_{SWS25} + \Delta pH_{SWS25\text{-}BA}$). 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. Further the comment that the DeltapHc term is in the order of _10-3, and therefore not so important, might not be true. You are reporting of trends in pH in that order of magnitude. In summary, a lot of confusing calculations are presented to come up with an adjustment (DeltapHc) that, according to the authors, has "a very small weight in pHc" and to me seems to be poorly justified scientifically in the first place. We hope to have cleared this up.

In the Result section I found it interesting that cLSW has experienced large acidification rates in spite of low ventilation the last decade or so. It would be interesting to read a few lines of thought on why that is. Besides the newly introduced comparison between our results and those from time series stations (ESTOC and BATS), there are several spots in the revised version where this aspect you highlight is discussed more fully (third paragragh on the discussion section): “…*The* $pH_{SWS25\text{-}BA}$ *decrease of the layers cLSW, uNADW and DSOW (Irminger basin), and SPMW and uNADW (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 uLSW (Irminger and Iceland basins) and cLSW (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* $pH_{SWS25\text{-}BA}$ *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...*”. It seems to suggest that the “acidification” due to respiration is more important than the uptake of Cant from the surface. In many instances these two effects are confused in the manuscript, and in the end I wonder if a fast ventilated water mass should be more affected by acidification, or a water mass whose ventilation rate has decreased. It the end it is a matter of balance between basically C_{ant} input, organic matter remineralization and photosynthetic activity. Such balance is specific to each water mass, and this is another of the reasons why we decided to opt following the main water masses in the NASPG over the years. For instance, in the beginning of the discussion the authors state that “ pH normally decreases with depth” (presumable due to respiration of organic matter -correct), and a few lines later they state that “surface water with lower average pH” is injected to depth explaining a mid-depth minima in pH. This was poorly expressed. This is how it is written now (first paragraph on the Results section): “…*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 (uNADW and lNADW). The branch of uNADW that spreads westward into the Iceland basin mixes with LSW (Yashayaev etl al., 2008) forming a pH gradient that shows decreasing pH values over time. The influence of LSW in the uNADW is also revealed by the imprint of LSW in the AOU and* $Si(OH)_4$ *values of the uNADW, which are lower those in the lNADW layer (Table 2c). In the Irminger basin the decreasing trends of* pH_{SWS25} *are clearly visible in the most recently ventilated waters like the uLSW 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.*”. Similarly, on page 3016 the authors state “The hampered ventilation from increased surface ocean stratification is expected to bring about a decrease in dissolved oxygen concentrations and pH levels, amongst other things because Cant would not be as effectively transported toward the ocean interior via deep convection and water mass formation processes (Perez et al., 2010).”. Why should pH decrease if LESS Cant is injected? Because surface stratification would facilitate the accumulation of more organic matter in the upper layers, and its oxidation would cause a drop of pH due to degradation of organic matter. There are basically three main components that affect the acidity of water masses: mixing with waters of different pH; synthesis-respiration of organic matter; and the influence of C_{ant}. The first two factors are the main causes of the natural variability of pH, while the C_{ant} influence belongs to the human induced variability. On the revised version we explore further the different contributions of these components to the observed acidification. As stated above, the C_{ant} storage rates provided by Pérez et al. 2010 have been used on the revised manuscript version to calculate the expected acidification rates due to human activities and compare these expected rates with our observation-based results, where no separation between the anthropogenic and natural acidification signals has been done (see the second paragraph in Section 4, "Discussion"). This way, it is possible to evaluate how much of the observed acidification in the different water masses is human-induced and how much is due to natural variability. This is what's on the third paragraph of the Discussion section in the revised manuscript: "…*The* $pH_{SWS25-BA}$ *decrease of the layers cLSW, uNADW and DSOW (Irminger basin), and SPMW and uNADW (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 uLSW (Irminger and Iceland basins) and cLSW (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* $pH_{SWS25-BA}$ *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.*". I don't question the statement, but the driver of the change has to something else, such as respiration.

Prediction of future pH values: Since such a big part of the discussion is devoted to this subject, why is the figure contained in the supplementary material? Thank you for this remark. We have done as you suggested and now Fig. S1 is an integral part of the main text (new Fig. 4). We have also deleted the references to the two CO_2 emission scenarios we mentioned to avoid complicating the main message. Our projections are based on xCO_2 values, not on time, or on how fast those xCO_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. Is a decrease in pH for cLSW of 0.45 units consistent with the thermodynamics of the carbonate system for a pCO2 of 775 ppm? Considering only the thermodynamics in such hypothetical (future) acidification process would not be appropriate, more so in the case of cLSW in the Iceland basin, where according to our results only 50% of the observed acidification rate is caused by C_{ant} entry. However, this case still seems to be consistent with the thermodynamics: if one calculates the expected C_T that cLSW would have under an atmosphere with 775 ppm of xCO_2, then one obtains an increase of about 100 $\mu mol\ kg^{-1}$ in C_T with respect to the average C_T of this water for the 2000s (~2150 $\mu mol\ kg^{-1}$). That increase in C_T can be expected to reduce pH by roughly 0.20 units (and this would be only the anthropogenic component of the acidification, i.e., about 50% according to our results). Can it be that the high trend for cLSW "acidification" is a result of low ventilation recently, and that if the cLSW becomes better ventilated in the future, waters with higher pH will dominate this water mass, so that your linear trends are wrong? One of the advantages of the time period studied here is that, in terms of NAO-driven ventilation (more ventilation during high-NAO index years, and vice versa; Pérez et al. 2010), it has undergone several different situations, and since our linear acidification trends come directly from the observations during those climatic conditions, we can have a high degree of confidence that the obtained trends (which turned out to be linear) are representative of different water mass ventilation scenarios. Adding to this, we provide the following evidence: In the early 90s (1989–1995) the 5-year mean ± standard deviation of this index was 3.3±0.8 indicating a high phase of the NAO. A low NAO phase period followed during the years 2002–2006, when the index value dropped to −0.1±0.6. Year 1996 is characterized by negative NAO, and 1997 to 2000 by moderate positive NAO. However, in spite of the variations of the NAO index during the study period, NAO was close to neutral (above and below, i.e., positive and negative indexes), and for our purposes the important point is exactly that: "*…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).*", as argued in the text. It seems to me that the high level of pH decrease in cLSW is due to respiration, which can change if the ventilation increases again. As mentioned in the above comment, acidification is a generally the result of the combined effects of C_{ant} entry, water mass mixing and of organic matter respiration. According to our analysis, in the case of cLSW it seems that the observed acidification is mostly due to the influence of C_{ant}, i.e., human-induced.

Minor / technical comments:

GENERAL COMMENT: Given that the manuscript has changed substantially (motivated by the reviewers' 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).

- Page 3004, line 26: What is excess anthropogenic CO2". When referring to a percentage, make very sure if you talk about fossil fuel emissions only, or if you include land use change, and also for which time frame you are presenting these numbers. They are all different. You are right. We meant simply anthropogenic CO_2, i.e., all CO_2 derived from human activities since the Industrial Revolution. The sentence has now changed: "*Roughly 20-35% of the anthropogenic CO_2 (C_{ant}) emissions are absorbed by the oceans (Khatiwala et al., 2009) mitigating the global warming.*".

- Page 3007, line 17. Do the authors mean "higher" precision rather than "lower"? Thanks. We meant higher precisions (better measurements). The sentence now is as follows: "*…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).*".

- Page 3008, line 18: What is "timely date"? We meant "convenient", because those two cruises were conducted in 1991 and filled the time gap between the TYRO (1990) and the OACES (1993). The sentence has been modified and now is as follows: "*…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 $A_T=S/35\cdot(2294.7+1.37\,[Si(OH)_4])$ ($R^2=0.97$; $[Si(OH)_4]$ 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.*".

- The normalization of alkalinity on page 3008 assumes a zero intercept, which has been shown by (Friis et al., 2003) to be flawed. I suggest changing this. The normalization to a common S=35 removes the A_T-S co-variation, compensates for freshwater balance effects and brings all surface waters close to conditions in lower layers. You are right in that this normalization scheme ("zero alkalinity at zero salinity") comes with certain caveats (according to Friis et al. 2003). However, the recommendations of alternative alkalinity normalizations in the work by Friis et al. 2003 refer to surface waters (upper 50 meter) rather than to the entire water column, which is where this equation was mostly applied in the case of the AR7E and A01E cruises, like in Pérez et al. 2010, where they use this same A_T expression ($A_T=S/35\cdot(2294.7+1.37\,[Si(OH)_4])$).

- Page 3009, line 3: Please avoid words like "exceptionally". Done. The authors seem to forget the southern ocean is the region where most of the Cant is taken up. Please note that this entire sub-section has been removed in the revised version. However you are right. When one looks at the C_{ant} budgets (the balance between atmospheric uptake, lateral advection and storage of C_{ant}) of the major ocean basins, the Southern Ocean is where most C_{ant} is taken up, but in the NASPG is where most C_{ant} is stored (Khatiwala et al., 2009;

Sabine et al., 2004).

- Page 3010, line 10: AOU does not "accurately" trace ventilation. You are right. This whole paragraph has been removed in the revised version of Section 2.2.2 (now 2.2.1). Strictly AOU traces respiration, and an assumption of constant respiration has to be made to convert AOU into ventilation. You are right.

- Page 3011, line 8. "Selected meteorological stations". State which ones. We replaced "selected" by "NASPG". We used the stations located in our study region (the NASPG), which can be easily identified on the map that's on the home page of the NOAA Carbon Cycle Greenhouse Gas group (provided on the text). The sentence now is as follows: "*…The xCO_2^{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)…*". Why you not use the well-known average CO2 concentration for the northern hemisphere. We wanted these data to be as local and accurate as possible.

- Table 1: The abbreviation "n.a." is often used for "not available", not for "no adjustment" as presented here. I suggest use "0" for no adjustment, and "n.a." for those cases where this parameter was not measured, or considered due to low quality. Done.

- Page 3012, line 15:"more acidic"?? The pH is about 7.7 in this water mass. This is well above neutral pH. More correct would be "less basic". You are right. Both ways of putting it are in fact right. "Less basic" is certainly more appropriate if one takes pH=7 as the reference for neutral pH, which is true for pure distilled water at 25 ºC and 1 atm. However if we consider as the reference or "baseline" the average ocean pH, which is around 8.1, then the "more acidic" tag is actually quite appropriate. This applies to a number of instances in this paper, for instance a few lines down on the same page; "NADW is natural acidic" – that is simply not true.

- Figure 2. Is it necessary to present pH sections for all the OVIDE lines? The advantage of the OVIDE section in this case is that it follows the very same track (which, on the other hand, gives representative coverage of the NASPG) over almost a decade, which is quite convenient in the context of the main objective in our study: to study the evolution of pH in the main water masses of the NASPG. You are hard pressed to visually see any differences, and you still don't know if differences you might see (such as in the deep Irminger Basin are due to variability in water masses rather than acidification. The new version of Fig. 2 now includes the isopycnals that delimit the studied water masses (also presented in Fig. 1b, in new Table 2 and in the main text). We hope this facilitates the visual follow of pH evolution, as you suggest. Also, Fig. 3 condenses all of that information in fewer points to give precisely that, a quantitative approximation to acidification rates. The difference between 1991 and 2008 is striking though. Yes indeed!

- Page 3014, line 5: The sentence starting with "Any of. . ." is unclear. What is the "maximum acidification rates achievable during 1981 to 2008". The sentence has been removed. FYI, it referred to the expected acidification rate that the water mass would have had due to C_{ant} entry and to its natural variability.

- Page 3014, lne 8: Iberian basin? Figure S1: Normally is the Omega value not given as percent. You are right, but we decided to express it as a percentage to make it easier for non-specialist readers to follow. Also, please notice that former Fig. S1 is now an integral part of the paper (new Fig. 4), since a good deal of the discussion section was based on it.

- Table 1: Which version of the TTO data is used? There is an updated version of the TTO data available, see (Tanhua and Wallace, 2005). We used the updated version that is publicly available in the CARINA dataset site: http://store.pangaea.de/Projects/CARBOOCEAN/carina/index.htm. That version of the TTO data was provided to the CARINA administrators / coordinators by the corresponding authors / P.I. of the cruise.

- Figure 3. In a recent publication by one of the co-authors of this study, the trend (in that case of Cant) was better fitted vs. the atmospheric perturbation of CO2 than vs. time. Why is that not done in this paper? That is what we did in former Fig. S1 (now Fig. 4). We have also deleted the references to the two CO_2 emission scenarios we mentioned, to avoid complicating the main message. Our projections are indeed based on xCO_2 values, not on time, or on how fast those xCO_2 values are reached (that depends on the emission rate / scenario). The reason we included the emission scenarios in the former version was to provide some context, but this seemed to blur the main message, so we decided to delete these references. It would at least provide some confidence check on the results, i.e. if the trends extrapolated to zero atmospheric perturbation is very different from a deltapH of zero, there might be a problem. Please, notice that the "baseline" (zero atmospheric perturbation) for such hypothetical "confidence check" would correspond to 280 ppm of xCO_2, not zero. Also, the y-axis in our graph shows pH, not a ΔpH, so the y-axis intercept would not be zero. It would be rather the preindustrial value of pH for cLSW and SPMW in the Iceland basin.

Observed acidification trends in North Atlantic water masses

M. Vázquez-Rodríguez[1], F.F. Pérez[1], A. Velo[1], A.F. Ríos[1], H. Mercier[2]

[1] Department of Oceanography, Instituto de Investigaciones Marinas (IIM), CSIC, Eduardo Cabello 6, E-36208 Vigo, Spain

[2] Laboratoire de Physique des Océans (LPO), CNRS Ifremer IRD UBO, IFREMER Centre de Brest, B.P. 70 29280 Plouzané, France

Corresponding author: M. Vázquez-Rodríguez (mvazquez@iim.csic.es)

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±0.0002 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±0.0002 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*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 CO_2 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 CO_2 (C_{ant}) emissions are absorbed by the oceans (Khatiwala 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 $A_T = S/35\cdot(2294.7+1.37\ [Si(OH)_4])$ ($R^2=0.97$; $[Si(OH)_4]$ 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 σ_θ = 45.84 kg m^{-3} and the upper NADW (*u*NADW) spreading in the density range $36.94 < \sigma_\theta < 45.84$ kg m^{-3}. We took the density range $37 < \sigma_\theta < 45.84$ 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 ($32.35 < \sigma_\theta < 37$ 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 $27.2 < \sigma_\theta < 32.35$ kg m^{-3} and the North Atlantic Central Water (NACW) layer is established from surface to $\sigma_\theta < 32.35$ 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 σ_θ = 27.6 kg m^{-3}. The upper and classical LSW (*u*LSW and *c*LSW) spread in the density ranges of $27.68 < \sigma_\theta < 27.76$ kg m^{-3} and $27.76 < \sigma_\theta < 27.81$ 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 $27.68 < \sigma_\theta < 27.76$ kgm^{-3}; between $27.76 < \sigma_\theta < 27.81$ kgm^{-3}, respectively. The North Atlantic Deep Water (NADW, which includes the ISOW contributions) is delimited by $27.81 < \sigma_\theta < 27.88$ kg m^{-3}, and the Denmark Strait Overflow Water (DSOW) by $\sigma_\theta > 27.88$ kg m^{-3} (Fig. 1b).

2.2.1 Basin normalization of average $\mathbf{pH_{SWS25}}$

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 $\Delta pH_{SWS25\text{-}BA}$. This term represents the deviation of the pH_{SWS25} (average from cruise data) from the $pH_{SWS25\text{-}BA}$ basin average (BA).

$$pH_{SWS25\text{-}BA} = pH_{SWS25} + \Delta pH_{SWS25\text{-}BA} \qquad \textbf{(1)}$$

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

$$\Delta \mathrm{pH}_{SWS25-BA} = \sum_{i=1}^{4} a_i \left(\mathrm{X}_i^{\mathrm{WOA05}} - \mathrm{X}_i^{c} \right) \qquad \textbf{(2)}$$

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 "*i*th" 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.

$$\mathrm{pH}_{\mathrm{SWS25}}^{\mathrm{MLR}} = \sum_{i=1}^{5} a_i \mathrm{X}_i^c + k \qquad \mathbf{(3)}$$

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= xCO_2^{atm} values used as input parameters in equation (3) are the averages for the year of the corresponding cruise "c". The xCO_2^{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 xCO_2^{atm} variable (Table 3) in equation (3) is not used in equation (2) since the $\Delta pH_{SWS25\text{-}BA}$ term should only include the effect of variables with spatial variation. Such xCO_2^{atm} terms are required when calculating the "a_i" coefficients (equation 3, Table 3), since xCO_2^{atm} has co-variation with pH_{25SWS}. 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 xCO_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 xCO_2^{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 (σ_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 etl 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 $Si(OH)_4$ values of the *u*NADW, which are lower 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 ($pH_{SWS25\text{-}BA}$), as described on section 2.2. The correction applied ($\Delta pH_{SWS25\text{-}BA}$) 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 $pH_{SWS25\text{-}BA}$ 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 20ºW. In general, we can see a trend of decreasing pH over time for both pH_{SWS25} and $pH_{25SWS-BA}$ 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 *u*LSW 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*LSW, *u*NADW 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 *u*NADW and *l*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 $pH_{SWS25-BA}$ 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±0.0001 yr^{-1}) and the *u*LSW (-0.0017±0.00004 yr^{-1}) (both in the Irminger basin), and the SPMW (-0.0012±0.0002 yr^{-}

^{1}) in the Iceland basin. The $pH_{SWS25\text{-}BA}$ of *c*LSW in the Iceland basin presents a remarkable average decrease of -0.0016±0.0002 yr^{-1}, unlike in the Irminger and ENA basins (-0.00089±0.00004 and -0.0008±0.0001 yr^{-1}, respectively). The layer of *u*NADW shows decreasing $pH_{SWS25\text{-}BA}$ vs. time trends from the Irminger (-0.0010±0.0001 yr^{-1}) to the Iceland basin (-0.0008±0.0002 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 $pH_{SWS25\text{-}BA}$ 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±0.0002 yr^{-1} (R^2 =0.15; p-value = 0.57) and -0.0003±0.0001 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±0.0001 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 (29º10'N, 15º30'W) and BATS (31º43'N, 64º10'W), in the Subtropical Atlantic. At the Irminger basin, the observed values of $pH_{SWS25\text{-}BA}$ decrease rates for SAIW and *u*LSW are -0.0019±0.0002 and -0.0017±0.0001 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 $pH_{SWS25\text{-}BA}$ decreasing rate of the NACW (-0.0009 ± 0.0001 yr^{-1}) is similar to the rates computed at the ESTOC site at 300 and 600 m (-0.0010 ± 0.0004 and -0.0008 ± 0.0003 yr^{-1}, respectively) for the decade 1995-2004 (González-Dávila et al., 2010). At 3500 m, the $pH_{SWS25\text{-}BA}$ rate of decrease for *l*NADW here obtained (0.0002 ± 0.0002 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±0.0002 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 ± 0.0003 yr^{-1}) slightly higher (considering the associated uncertainties) than our pH rate (-0.0006±0.0001 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 $pH_{SWS25\text{-}BA}$ 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 $\left(\partial pH/\partial t\right)_{ANT} = \left(\partial C_{ANT}/\partial t\right)\left(\partial pH/\partial C_T\right)_{(S,A_T)}$, where $\left(\partial pH/\partial t\right)_{ANT}$ is the expected variation over time of human-induced pH (due to C_{ant}); $\left(\partial C_{ANT}/\partial t\right)$ is the corresponding C_{ant} storage rate (from Pérez et al., 2010); and $\left(\partial pH/\partial C_T\right)_{(S,A_T)}$ 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 $pH_{SWS25\text{-}BA}$ 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 $pH_{SWS25\text{-}BA}$ 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 $pH_{SWS25\text{-}BA}$ 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 $[CO_3^{2-}]$ 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 xCO_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 xCO_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 $\Omega_{arag} = [Ca^{2+}][CO_3^{2-}]/K_{sp}^{'}$, where square brackets indicate seawater ion concentrations and $K_{sp}^{'}$ is the apparent solubility product of aragonite (Mucci, 1983). Because $[Ca^{2+}]$ is highly and positively correlated with salinity, Ω_{arag} is largely determined by variations in $[CO_3^{2-}]$. 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 xCO_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 (Ω_{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*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 Ω_{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 ~0.2 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 ºC 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*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±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.

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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 μmol kg^{-1} for C_T and A_T.

Table 2 Temporal evolution (1981-2008) of the (average±standard error) values of salinity, potential temperature, AOU, silicate concentrations, measured pH (pH_{SWS25}), pH basin-corrections ($\Delta pH_{SWS25\text{-}BA}$) and basin-normalized pH ($pH_{SWS25\text{-}BA} = pH_{SWS25} + \Delta pH_{SWS25\text{-}BA}$) 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 xCO_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 xCO_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 ±2 μmol·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 ±4 μmol·kg^{-1}.

Table 2a. Irminger Basin

Year	Salinity	θ (ºC)	AOU (μmol·kg^{-1})	Si(OH)$_4$ (μmol·kg^{-1})	pH $_{SWS25}$	ΔpH $_{SWS25\text{-}BA}$	pH $_{SWS25\text{-}BA}$
SAIW (σ_0 <27.68 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	*	*	*
***u*LSW** (27.68 < σ_0 <27.76 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	*	*	*
***c*LSW** (27.6 < σ_0 <27.81 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	*	*	*
***u*NADW** (27.81 < σ_0 <27.88 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 (σ_0 >27.88 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

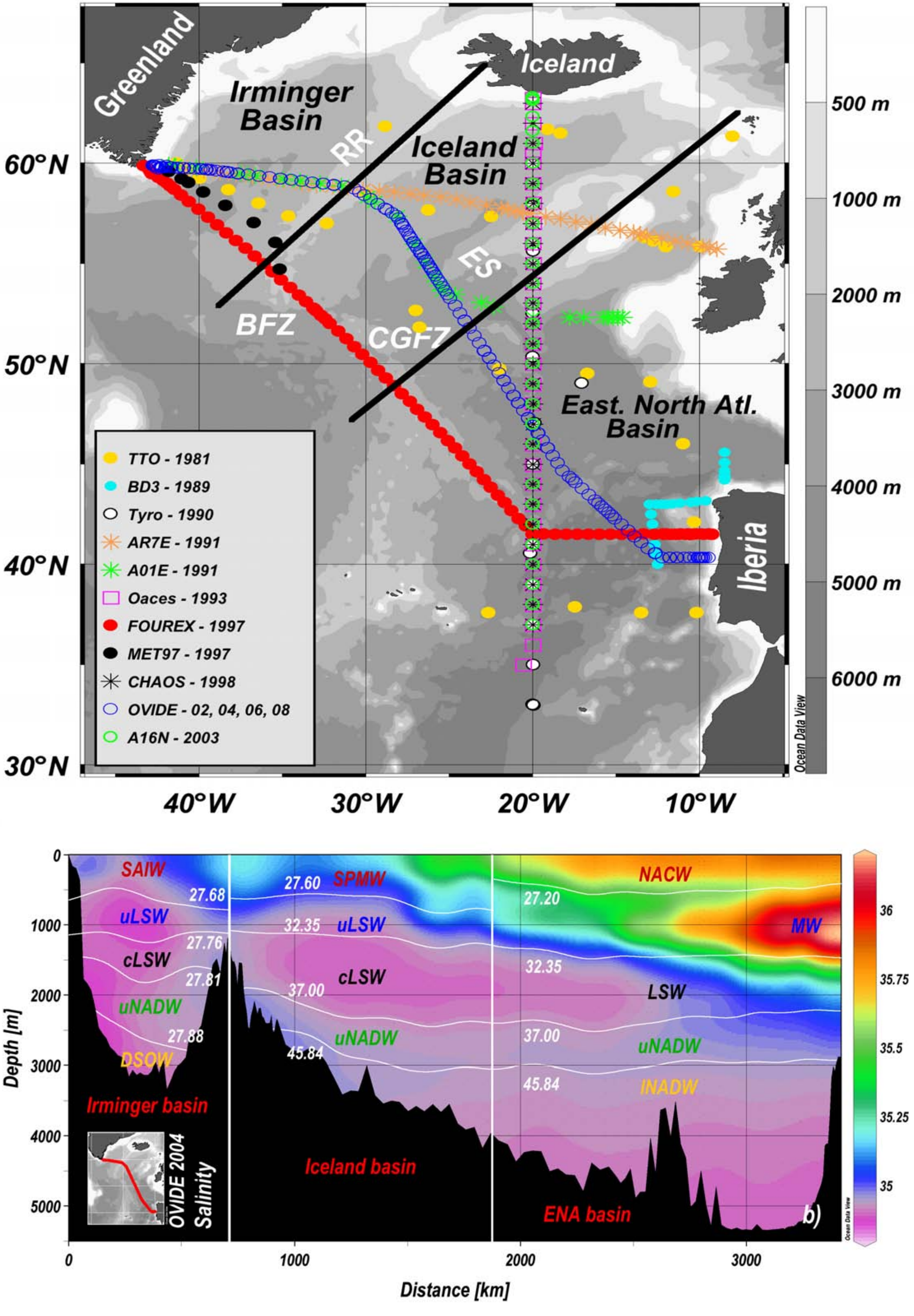
Year	Salinity	θ (ºC)	AOU (μmol·kg^{-1})	Si(OH)$_4$ (μmol·kg^{-1})	pH$_{SWS25}$	ΔpH $_{SWS25-BA}$	pH $_{SWS25-BA}$
SPMW (σ_0 <27.60 kg m^{-3})							
1981	35.183 ± 0.001	8.242 ± 0.003	28.2 ± 0.1	6.89 ± 0.04	7.814 ± 0.001	-0.008 ± 0.005	7.806 ± 0.005
1991	35.109 ± 0.001	7.030 ± 0.003	22.9 ± 0.2	7.73 ± 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	*	*	*
***u*LSW** (σ_0 >27.60 kg m^{-3}; σ_1 <32.35 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	*	*	*
***c*LSW** (σ_1 >32.35 kg m^{-3} ; σ_2 <37.00 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	*	*	*
***u*NADW** (σ_2 >37.00 kg m^{-3} ; σ_4 <45.84 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

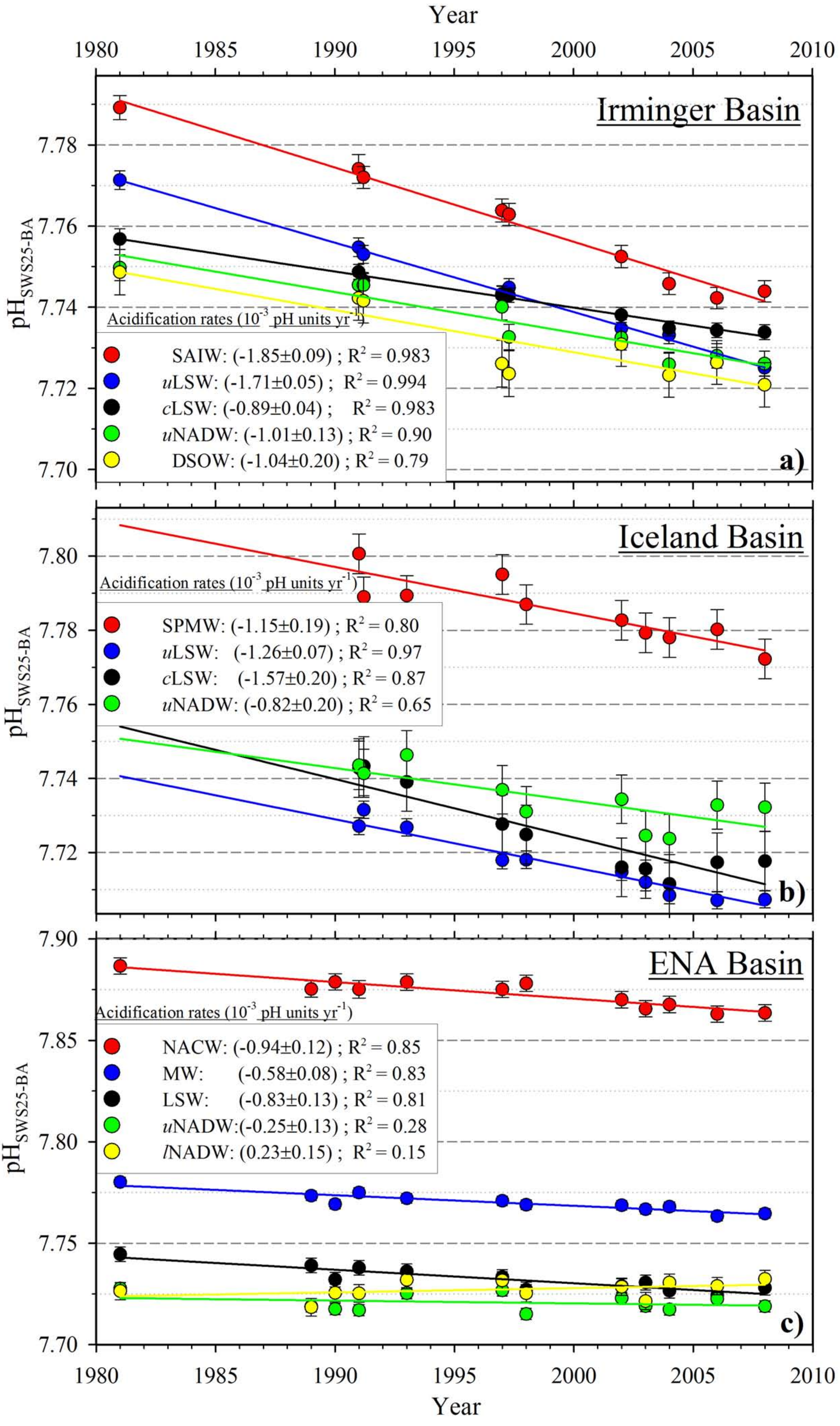
Year	Salinity	θ (ºC)	AOU (μmol·kg^{-1})	Si(OH)$_4$ (μmol·kg^{-1})	pH $_{SWS25}$	ΔpH $_{SWS25-BA}$	pH $_{SWS25-BA}$
NACW (σ_0 <27.20 kg m^{-3})							
1981	35.618 ± 0.001	12.472 ± 0.003	27.5 ± 0.2	3.74 ± 0.05	7.883 ± 0.001	0.004 ± 0.004	7.887 ± 0.004
1989	35.661 ± 0.001	12.448 ± 0.004	23.6 ± 0.2	2.86 ± 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 (σ_0 >27.20 kg m^{-3}; σ_1 <32.35 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 (σ_1 >32.35 kg m^{-3} ; σ_2 <37.00 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	*	*	*
***u*NADW** (σ_2 >37.00 kg m^{-3} ; σ_4 <45.84 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	*	*	*
***l*NADW** (σ_4 >45.84 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

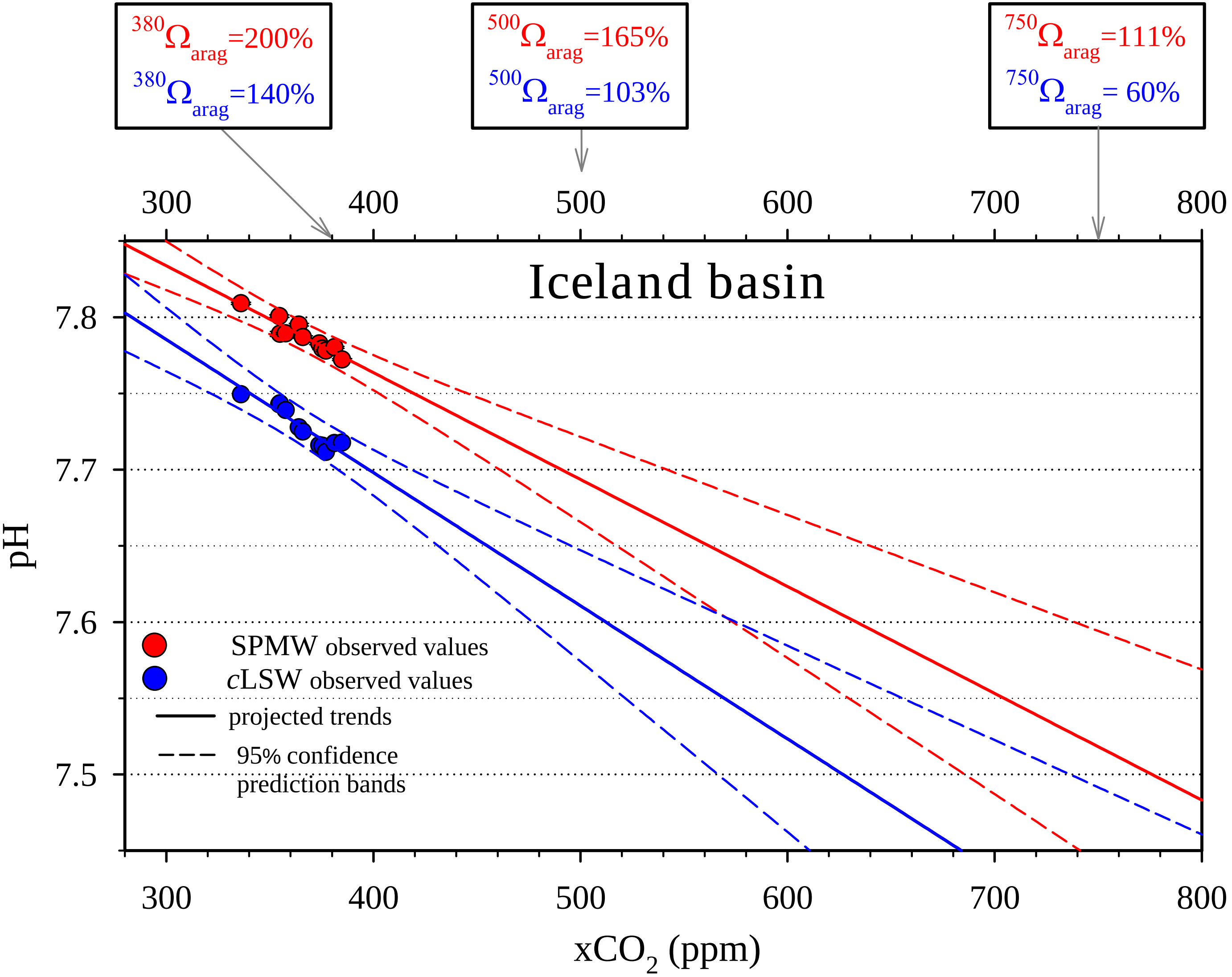
Table 3.

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 ; ºC^{-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
*u*LSW	0.99	0.002	-0.95 ± 0.04	-11 ± 1	n.s	30 ± 10	0.67 ±0.08.
*c*LSW	0.99	0.002	-0.50 ± 0.04	-17 ± 3	n.s.	97 ± 16	0.44 ±0.14.
*u*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.
*u*LSW	0.96	0.002	-0.72 ± 0.06	-7 ± 2	n.s.	n.s.	n.s.
*c*LSW	0.81	0.006	-0.95 ± 0.21	-11 ± 6	n.s.	-40 ± 24	n.s.
*u*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.
*u*NADW	0.78	0.003	n.s.	n.s.	-2.3 ± 0.6	27 ± 11	-3 ± 1
*l*NADW	0.28	0.004	0.13 ± 0.10	n.s.	n.s.	20 ± 13	n.s.


Greenland
Iceland
Irminger Basin
Iceland Basin
RR
ES
BFZ
CGFZ
East. North Atl. Basin
Iberia
60°N
50°N
40°N
30°N
40°W
30°W
20°W
10°W
500 m
1000 m
2000 m
3000 m
4000 m
5000 m
6000 m
Ocean Data View
● TTO - 1981
● BD3 - 1989
○ Tyro - 1990
✳ AR7E - 1991
✳ A01E - 1991
□ Oaces - 1993
● FOUREX - 1997
● MET97 - 1997
✳ CHAOS - 1998
○ OVIDE - 02, 04, 06, 08
○ A16N - 2003
SAIW
SPMW
NACW
uLSW
cLSW
uNADW
DSOW
MW
LSW
lNADW
27.68
27.76
27.81
27.88
27.60
32.35
37.00
45.84
27.20
Irminger basin
Iceland basin
ENA basin
OVIDE 2004
Salinity
b)
Depth [m]
Distance [km]
0
1000
2000
3000
4000
5000
36
35.75
35.5
35.25
35


a)
A01E 1991
OACES 1993
SAIW
SPMW
NACW
uLSW
cLSW
LSW
MW
uNADW
DSOW
lNADW
Irminger basin
Iceland basin
ENA basin
7.75
7.775
7.875
7.825
7.735
7.725
b)
OVIDE 2002
c)
OVIDE 2004
d)
OVIDE 2006
e)
OVIDE 2008
7.9
7.85
7.8
7.925
Depth [m]
0
1000
2000
3000
4000
5000
Distance [km]
0
500
1000
1500
2000
2500
3000
7.95
7.9
7.85
7.8
7.75
7.7
Ocean Data View


Year
1980
1985
1990
1995
2000
2005
2010
Irminger Basin
$pH_{SWS25-BA}$
7.78
7.76
7.74
7.72
7.70
Acidification rates (10^{-3} pH units yr^{-1})
SAIW: (-1.85±0.09) ; R^2 = 0.983
*u*LSW: (-1.71±0.05) ; R^2 = 0.994
*c*LSW: (-0.89±0.04) ; R^2 = 0.983
*u*NADW: (-1.01±0.13) ; R^2 = 0.90
DSOW: (-1.04±0.20) ; R^2 = 0.79
a)
Iceland Basin
$pH_{SWS25-BA}$
7.80
7.78
7.76
7.74
7.72
Acidification rates (10^{-3} pH units yr^{-1})
SPMW: (-1.15±0.19) ; R^2 = 0.80
*u*LSW: (-1.26±0.07) ; R^2 = 0.97
*c*LSW: (-1.57±0.20) ; R^2 = 0.87
*u*NADW: (-0.82±0.20) ; R^2 = 0.65
b)
ENA Basin
$pH_{SWS25-BA}$
7.90
7.85
7.80
7.75
7.70
Acidification rates (10^{-3} pH units yr^{-1})
NACW: (-0.94±0.12) ; R^2 = 0.85
MW: (-0.58±0.08) ; R^2 = 0.83
LSW: (-0.83±0.13) ; R^2 = 0.81
*u*NADW:(-0.25±0.13) ; R^2 = 0.28
*l*NADW: (0.23±0.15) ; R^2 = 0.15
c)
1980
1985
1990
1995
2000
2005
2010
Year



$^{380}\Omega_{arag}$=200%
$^{380}\Omega_{arag}$=140%
$^{500}\Omega_{arag}$=165%
$^{500}\Omega_{arag}$=103%
$^{750}\Omega_{arag}$=111%
$^{750}\Omega_{arag}$= 60%
300
400
500
600
700
800
Iceland basin
7.8
7.7
7.6
7.5
pH
SPMW observed values
*c*LSW observed values
projected trends
95% confidence prediction bands
300
400
500
600
700
800
xCO_2 (ppm)