REVIEWER #1

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

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

Dear reviewer,

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

1) Methods section: Section 2.2 where the averaging and basin normalization of data is described is more concise now and makes clear that such data treatment does not aim at separating the anthropogenic and the natural acidification signals (this was not explained well enough in the previous version of the manuscript), but rather calculate small pH corrections to the measurements ($\Delta pH_{SWS25\text{-}BA}$) 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

GENERAL COMMENTS

Vazquez-Rodgriguez et al. have collected pH data, or data from which pH could be calculated, in a sequence of repeated or quasi-repeated cruises between Greenland and the Iberian Peninsula spanning roughly the last 30 years. After careful consideration of the type of data available, they assemble a coherent and calibrated dataset of pH values. After binning and averaging these data in representative isopycnal layers, they isolate generally decreasing pH trends in these layers over the period analyzed. Their main result is a set of regionally-specific acidification rates for the North Atlantic derived from direct interior carbon parameter measurements.

While the overall trends are likely robust, the presentation of this paper would benefit from significant improvements and a more thorough analysis and discussion of the results. These are obviously important data to publish and the data set has a lot of potential and will have many uses for the community, but the current form and content of this manuscript is insufficient, in my opinion, to warrant publication in Biogeosciences at this point. In contrast to pervious papers published by the same group on the same data set and their recognized expertise on these sections, this particular manuscript lacks depth of interpretation.

As mentioned above, we have made major modifications to the Methods and discussion sections. More details are given below, in the specific comments.

As it stands, based on the description provided in the text, it is difficult for the reader to follow the calculations and not easy to evaluate the results presented in this manuscript Section 2.2, the results and the discussion sections have been largely modified to make them clearer, more concise and easier to follow the ideas. One aspect of the paper that can be greatly improved is the structure of the paragraphs and the sequence in which the ideas are presented. When reading, it is not always clear where the authors are going. Technical language can be approximate (e.g. the treatment of mixing, advection, ventilation, convection) This has been corrected throughout the manuscript and statements are often too general or not fully substantiated. Some suggestions are provided in the "Technical comments" section below, although these comments should not be viewed as an exhaustive list, as much of the paper should be revisited and the scientific focus of this study, in light of its unique dataset (not generalities about the issue of ocean acidification), should be made clear. The modification of the manuscript has been done keeping with this one aspect at the forefront: focusing on the analysis of the results obtained from our dataset, and comparing them with other studies when possible.

Many part of this paper also appear to be nearly identical to Perez et al. 2010 (cited on p3024, line 11-13), a paper that discussed anthropogenic carbon results along the same set of sections. Clearly pH is a different variable than Canth and I understand that the cruise tracks are the same, but much of the paper re-uses/paraphrases content in Perez et al. 2010. We refer to this work more often in this version, to avoid repeating things. For this reason, I would expect that many of the generalities of the dataset already published in earlier references would not be repeated here and that this space would be used instead to extend the analysis of the result. This has been done. For instance a quick survey of similarities with Perez et al. 2010 shows that:

- Table 1 is identical to that in Perez et al. 2010, with the addition of OVIDE2008. While most of the cruise information on this table is the same as in Pérez et al. 2010 (except for OVIDE 2008), there are two columns which are specific to our study (the "pH" and "Uncertainty" columns). In any case, we think this information is necessary for the reader, and referring to another work would not make any easier the reading of the manuscript. Section 2.1 is thus also very similar to paragraphs in Sec 2 in Perez et al. 2010. The entire section 2 has been fully revisited and shortened considerably, and there are more occurrences of the reference to Pérez et al. 2010.

- This paper also presents very related data, that is the increase in Canth in the same layers treated in this paper. The main difference, as you pointed earlier, is that we look at a totally different variable and issue: pH (which is a direct measurement) and not anthropogenic CO_2 (that needs to be estimated from the measurements). There are processes that affect pH and not C_{ant} and viceversa, that is why this study is relevant and legitimate. However, in this version we have used the fact that Pérez et al. 2010 refer to the same water masses we do, to improve our discussion section. We have calculated the expected pH change due to the entry of C_{ant} in each layer, using the C_{ant} storage rates in Pérez et al. 2010, and compared the results with the acidification rates we obtained.

- Figure 1 is also identical to Perez et al. 2010, with the addition of OVIDE2008. Like in the case of Table 1, we think this figure is necessary to introduce the reader to the region of study and to how we looked at the water column of the NASPG, and referring to Pérez et al. 2010 would not improve the reading of the manuscript.

- Sec 2.2.2 is also very similar to Perez et al, 2010, section A2. As mentioned above, this section has been considerably shortened and modified and, while still being self-contained, it now relies more on previous works that have used a similar methodology (Pérez et al, 2010; Ríos et al., 2012).

SCIENTIFIC COMMENTS

Section 2.2.2 “Normalization and averaging of pH” is particularly confusing. This is clearer in Perez et al. 2010. This section has been considerably shortened and modified. This section describes a methodology to remove the effect of natural variability from the total signal. 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. It is not clear what is being accounted for by the correction proposed, however. A deeper analysis of this correction factor and a better presentation would greatly help the paper. We hope we have achieved this. 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.

The value of Table 2 is also not clear. The averaged pH values are presented in Supplementary Tables 1-3. I would rather see the supplementary tables in the main part of the paper and Table 2 in the supplement as Table 2 only contains intermediate results used to calculate the pH corrections, whose influences are not clear. All tables are now part of the main text. New Table 2 (formerly supplementary tables 1, 2 and 3) 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 ($pH_{SWS25\text{-}BA} = pH_{SWS25} + \Delta pH_{SWS25\text{-}BA}$). Overall, the manuscript would also benefit from a description of how errors are treated and a discussion of these errors (Done. In section 2.2 it is now explained what the errors represented in Fig. 3 are: “*…The error bars on the graph represent the error of the mean and the uncertainty due to the normalization of the data…*”) and a proof of concept application, perhaps on made-up data with known spatio-temporal variability, would help in convincing the reader that this approach in fact does recover the signal that is to be interpreted. This has been done by including the values of pH_{SWS25}, $\Delta pH_{SWS25\text{-}BA}$ and $pH_{SWS25\text{-}BA}$ on new Table 2, and also comparing our acidification rates with those in previous studies that used data either from time series stations like ESTOC or BATS (Santana-Casiano et al., 2007; González-Dávila et al., 2010; Bates et al., 2012), or from cruises

(Olafsson et al., 2009). It can be seen from there that our results not only are on the same order of magnitude as in the aforementioned studies, but they are also quite similar in magnitude most of the time (where comparison is possible), which supports the treatment of our data.

The authors should also provide a general discussion of the ΔpHc elements. It would be interesting to gain some insight into the natural variability of pH along this section. Maybe a section showing expected ranges in pH changes due only to changes in water mass mixtures using the mean pH of relevant water masses would be good. This would provide some context to evaluate the magnitude of the pH changes reported in relation to the potential pH changes. An assessment of how much natural variability is captured by these ΔpHc elements is necessary. As explained above, the normalization of pH data did not intend to separate the natural and the anthropogenic components of acidification. Nevertheless, as mentioned in the above comment, the inclusion of the $\Delta pH_{SWS25\text{-}BA}$ elements in new Table 2 and the updated description of data treatment in Section 2.2.1 provide the information requested in this comment. Additionally, 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.

A discussion of how volume (or area given its on sections) contained between isopycnal layer changes in time and how this affects the different components of pH would also be interesting (some of this is available in Perez et al. 2010). This analysis is done in Pérez et al., 2010, as you point out, and that is why we only refer to this work when necessary rather than give the same analysis and explanations again, as you have suggested when making reference to Section 2.2, Fig. 1 or Table 1. It seems also limiting to work with a small set of isopycnal layers as done here. Why not use more layers and present the results as vertical profiles in density interval instead of just picking a few layers to present on Figure 3. The selected isopycnals delimit the main water masses in the NASPG. In addition, by using the same isopycnal layers as in Pérez et al. 2010 we could use the C_{ant} storage rate data they provide and use it to compare our acidification rates with the pH rates expected from C_{ant} influence, and this is an added value to the discussion. What do the other layers show (at least show the acidification rate in Table 2 for all layers)? All acidification rates are listed in the text and in the inserts in Fig. 3. Is there a flux from one layer to the next? Some statements about dominant mechanisms (advection vs vertical mixing) are made, but there is no quantitative calculations made in that paper that support this. The data necessary to make this kind of computations is not part of our dataset. There are studies that have focused on these specific aspects of NASPG circulation (Lherminier et al., 2010; Thierry et al 2008; Ríos et al., 1992; Kieke et al., 2007; Yashayaev et al., 2008) and provide a level of detail in their analysis that is certainly not within the scope of our study. We have only made the necessary references when needed.

Some interesting discussion elements are mentioned but not treated thoroughly enough (e.g. NAO, subsurface intensification of acidification through LSW, effect on the lysocline). It is also stated that biology influences pH. What are the effects of photosynthesis and North Atlantic blooms on the data? Is that signal taken out totally from the calculation of pHc*? As explained before, the data normalization in Section 2.2 has nothing to do with this. Mixing is mentioned, but pH does not mix linearly as a quantity (equal part mixing between two water masses with pH1 and pH2 is not equal to (1/2)(pH1+pH2), and in fact the mixture will be closer to the more acidic water mass): it is the concentration of proton that mixes linearly. This is true, but we haven't performed any water mixing analysis in our analysis, or tried to obtain a pH value in such a way. In the context of mixing of different water masses, such as the situation in the North

Atlantic, what is the magnitude of this non-linear effect of water mass mixing? Our results are based on observations, not on water mixing analysis. Whenever we mention the effect of mixing or convection on pH is to try to account qualitatively (and supported from the literature) for the obtained results. Given variability in the strength of the overflows and in the formation of LSW, does this non-linear acidification effect due to mixing matter on these layers? Again, water mass analysis is not one of the goals of our study. The main objective is to provide quantitative information from observations of the acidification trends in the NASPG over the last three decades. However, I would expect that since the anthropogenic CO_2 influence on pH rates in these water masses is so big, given the strong vertical convection that occurs during their formation processes, and their pH is already considerably lower than the surrounding water masses, dyapicnal mixing would have a minor effect on the average pH values we are dealing with in our analysis.

TECHNICAL COMMENTS:

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

Below is a list of comments, questions and suggestions regarding the writing and also regarding the content. I tried to point out where I got hung up and where some of the flow of the text could be improved. I hope these will help the authors improve their manuscript.

Abstract:

****p3004**
l12-13 Why ‘surprisingly’? This has been deleted.

l14 ‘unprecedented’ – since these are the first measurements, it’s hard to make any statement like that. Thanks. This was misleading and it has been deleted.

l18. Linear Corrected.

l20. ...by the time atmospheric CO2 concentrations double the present ones. Does this statement depend on emission rates and ventilation rates? We referred to a specific atmospheric xCO_2 value, i.e., about twice the current pCO_2. Obviously, depending on the emission rates any given pCO_2 will be reached sooner or later. In any case, since we found the way to express it was misleading, we changed it to: “*...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 over ~775 ppm.*”

1. Introduction:

l22. ...is well known and researched. Perhaps just say 'is known' Done

l23. remove ',' before but Done

l23. 'its' as written would refer to 'the chemistry'. Restructure sentence. This sentence has been fully removed.

l26. 'quenched'. word choice. Replaced by “absorbed”.

**p3005

l1. 'hampering'. word choice. Replaced by "mitigating".

l4. remove 'the so-called' This sentence has been fully removed.

l5. sea-surface's should be sea-surface Done.

l5. 'on' pH, should be 'in' pH Sentence changed to "*…30% increase in hydrogen ion concentrations [H^+] (Caldeira and Wickett, 2005; Raven et al., 2005).*".

l5-6. '30% reduction in pH (0.1 units...)' Ocean pH is about 8, 30% of 8 is not 0.1. I don't understand this statement. Sentence changed to "*…30% increase in hydrogen ion concentrations [H^+] (Caldeira and Wickett, 2005; Raven et al., 2005).*".

l9-10. ...,and it is the onset... maybe best to replace by 'is thought to be the onset...' Done.

l11. 'Ocean acidification has a medley of juxtaposed...' word choice/style. Rewrite sentence. Done: "*Ocean acidification generates a combination of contrasted impacts on the marine environment (Doney et al., 2009)…*"

l20-21. 'the water mass formation processes abound...' Just before it says 'deep convection'. It is not clear what these 'formation processes are'. Rewrite sentence, be more specific. The whole paragraph has been rewritten: "*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 those water masses suffer changes in [H^+].*".

l23. 'turn the NASPG into the most effective entrance portal'. Is 'effective' defined as the amount of CO2 taken up divided by the number of Sverdrup formed? This has been removed (see answer to previous comment) What about the Southern Ocean? We don't deal with the Southern Ocean, just with the North Atlantic subpolar gyre.

l24. 'The negative feedback...' This sentence does not seem to fit in this paragraph. The whole paragraph has been deleted. It represented just some background information that did not help in getting the focus to the main goal of the manuscript ("*…examines the temporal variability of pH in the main water masses of the North Atlantic from direct observations…*").

l28. 'There are relatively few spots...' It would be informative to give a list of where this is possible. We do not think this would add any relevant information to the prospective reader. This can be checked from any publicly available dataset like GLODAP, CARINA, etc., and it is generally accepted in the bibliography (we cited the work from Wootton et al., 2008). The list would be short in the context of the global ocean (which is what we mean in our sentence here) but still long to include in the context of this paragraph. Most of this spots are just that, spots where there is a time series station (like BATS or ESTOC), or local studies from small cruises that have the purpose of monitoring the carbon system of one particular area, but there are certainly not many entire ocean regions (like the NASPG) where high-quality carbon data are available for a study of long-term trends.

****p3006**

l5-9. *General comment on the style of the introduction.* This is the only sentence that actually introduces the paper. It would be best to rewrite/reorganize the introduction section; it doesn't flow well as written now – it describes acidification but not much the rationale for this particular study. As written, it is not clear why this analysis was done or what the strengths of it are. The scientific goal of this study is not clear from the introduction. Done. We have shortened the introduction eliminating ancillary information that was not fundamental to lead to the main objective of the manuscript, which is still the same and is made explicitly clear: "*…examines the temporal variability of pH in the main water masses of the North Atlantic from direct observations*". Basically on the first paragraph of the introduction we put in context what the ocean acidification is (main topic of our study) and what's been causing it. The second paragraph gives some information on the circulation in the NASPG (our study region) and why this makes it potentially so susceptible of getting acidified. The third and last paragraph of the introduction explains what the aim of the study is, and the relevance of making such study from direct observations, not through numerical models.

l6. 'as well as its drivers'. It would be helpful to give a bit of information about what these drivers are and how they will be evaluated and in which sequence in the main text. We have deleted this sentence. The main drivers are anthropogenic CO_2 uptake and NASPG circulation and water mass formation, but these are elements that are relevant only once the discussion is started, when trying to explain the acidification rates obtained, which are the main objective of the study.

l7. '...high-quality, NASPG-covering carbon...' replace by 'high-quality carbon system data covering the NASPG between ...' Done.

2. Dataset and methodology

2.1 Dataset

l12. 'the relatively recent introduction' just say 'the introduction' This paragraph has been deleted in the new version.

l13. 'allowed making fast and yet very accurate' just say 'allowed for fast and accurate' This paragraph has been deleted in the new version.

l14. 'filling the need of improving and enlarging...synthetic data get tested'. Style/english, rewrite sentence. This sentence has been deleted in the new version. What are 'synthetic data'? data from models Is pH used as a model diagnostic ever? This sentence is maybe not needed. Just start paragraph with 'A total of fourteen...' and then insert a sentence 'pH was measured ...' and remove reference to models and synthetic data. Done. This is how Section 2 starts in the new manuscript version.

l18. 'spans over 27 years', just say 'spans 27 years' Done. The sentence has been moved to the first paragraph in section 2.2.

l21. 'have been established' replace by 'are defined by the main...' Done.

l25. rewrite 'Eastern North Atlantic (ENA) basin' Done. But the sentence moved. It is at the top of the first paragraph in section 2.2.

****p3007**

l1. 'Cruise data can be accessed', remove 'used here' Done. But the sentence moved. It is at the top of the first paragraph in section 2.1.

l5. Awkward sentence. Suggestion: '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).' Done. But the sentence moved. It is on the second paragraph in section 2.1.

l7. 'only bottle data of the inorganic carbon system WERE used'. This sentence has been removed.

l8. 'all the measurement are compliant with the latest ... recommendations...' How can that be true for data measured prior to the introduction of Certified Reference Material? Or be more specific of what 'compliance' means. Thanks for this remark. This sentence was too general and has been deleted. Instead, the quality and precision of the data are described specifically (Table 1 and second and third paragraphs on new section 2.1).

l12-17. Rewrite. Suggestion: 'Periodical checks of pH measurement precision with Certified Reference Material during the FOUREX and OVIDE cruises indicated a precision better than the 0.002 pH unit error reported by Clayton and Byrne (1993) and Millero (2007).' Done.

l20. '...constants for HF and HSO4-.' Indicate in Table 1 where these calculations were necessary. This part of the data analysis is now included in section 2.1 (second paragraph): "*…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).*".

l23-24. 'The use of ... identical acidity'. Rewrite sentence. Does that mean pH differences smaller than 0.01 cannot be detected because of the errors involved in rescaling all measurements to the same pH scale? This sentence has been replaced by "*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)*". Anyway, what the original sentence meant was that given two samples with identical [H$^+$], if one expresses the pH of sample 1 in SWS and the pH of sample 2 in a different pH scale (total, NBS…), then the value of pH could differ by up to 0.01 pH units, even though [H$^+$] is the same in both samples.

l26. 'Some of the cruises...' would be helpful to indicate which ones on Table 1. Also perhaps add another column to Table 1 with measurement accuracy and measurement/assessment technique. Done.

l26 to p3008, l2. This sentence does not belong this paragraph. This paragraph is about how Alk and DIC were measured. The sentence has been removed.

****p3008**

General comment. Again, the whole section 2.1. is not very well organized. Much of this information could be summarized in an expanded version of Table 1. The whole section has been rewritten.

**p3009

2.2 pH data analysis

2.2.1 Water mass approach

l3-4. Reference needed for that statement, linking the strength of anthropogenic CO2 uptake with the process of convection. Old section 2.2.1 has been deleted. This aspect of the methodology had been clearly explained in Pérez et al. 2010, to which we make several references in the revised version. The references were given in the old version of the manuscript, in the next sentence: (Azetsu-Scott et al., 2003; Pérez et al., 2008, 2010; Yashayaev et al., 2008).

l5. Please explain how convection changes carbon chemistry? Old section 2.2.1 has been deleted. Only FYI, this had to do with the uptake of C_{ant} during water mass formation processes.

l9-10. Say what is being followed exactly (e.g. alkalinity, etc.) instead of saying 'carbon system parameters' Old section 2.2.1 has been deleted.

l12. 'alleviate' the mixing problem, instead of 'avoid' would be a better word choice. Density compensating changes could occur. Section 2.2.1 is a lot of words to say that the data were analysed between isopycnals. It also does not justify the 'water mass approach' very clearly. Isopycnal analysis is rather routine nowadays. A whole section to say that seems superfluous. Old section 2.2.1 has been deleted. A brief description of the physical oceanography of the region and how the isopycnals chosen are related to circulation and climatology would seem more appropriate and would help with the results section. This has been done on the second paragraph of section 2.2.An overview of the mean acidity of the water masses in the region and the reason for these differences in acidity would also be welcome. There are climatologies available for other oceanographic variables, but not for pH. Our study provides a set of pH values in different water masses over different years that could be used as references in future studies in the NASPG.

2.2.2 Normalization and averaging of pH data

GENERAL ANSWER TO THE COMMENTS ON THIS SECTION: This whole section (now 2.2.1) has been restructured and rewritten aiming for clarity and conciseness. Please, refer to new section 2.2.1 and answers to previous comments.

Overall, this section is the hardest to follow. It needs some restructuring and a little more detail, especially a clearer explanation of the rationale behind the calculations.

l22-23. Were climatological averages calculated on isopycnals? Yes, for temperature, salinity, dissolved oxygen and nutrients (from WOA05 data). Those values were given in the supplementary tables (now Table 2) and are also necessary input parameters for equation 2.

l24-25. Instead of 'per water mass', is would be best to say 'between isopycnal layers and per year'. This sentence (first sentence of new section 2.2.1) has been rewritten: "*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}".

l25. Is the fundamental reason for doing the isopycnal and annual binning only because of convenience in plotting? Please refer to the explanation given in point 1) on the first page of this

reply letter. What effect does this averaging has on the final results? Please refer to the explanation given in point 3) on the first page of this reply letter Would using different layers change the analysis? The analysis would be the same, but referenced to different water bodies. Is there a significant temporal summer bias in the distribution of the data? This type of seasonal bias in the sampling is one of the things that the basin normalization described on section 2.2.1 tries to avoid / compensate.
l26-27. Does this approach in fact work to fix the representativeness problem? Much of the circulation is across the sections analyzed, not along the section. What guarantee is there that data from one side of the section are representative of the conditions on the other side. There is for instance an east-west gradient in alkalinity below the Mid-ocean Ridge. Other tracers, such as nutrients, salinity and temperature also have strong east-west gradients. This type of spatial bias in the sampling is one of the things that the basin normalization described on section 2.2.1 tries to avoid / compensate.

****p3010**

l1-3. A statement is made that natural variability must be removed. How much of an effect does natural variability have on pH in this region? How different would the analysis presented here be if natural variability were not dealt with? I feel it would be informative to see the contrast, if any. This point has already been discussed in several previous answers, for instance, in points 1) on the first page of this letter.

l10. The sentence has been removed. I'm not sure what 'ventilation ... can be traced' means. Should it be 'ventilation pathways ... can be traced'? or can ventilation rates be calculated? It meant followed or calculated.

l10. Given the different interpretation of ventilation, the term 'accurately' is a very subjective statement. This paragraph has been removed. As discussed earlier, 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).

l12. Briefly describe 'atmospheric molar fraction', how it is calculated/measured. It is not immediately clear or intuitive how what seems to be an atmospheric measurement can be used to trace a water mass in the interior without complications due to air-sea exchange, etc. Is this section supposed to justify the tracers used in the MLR? Its not immediately clear that this is the case. This paragraph has been removed. Please, refer to new section 2.2.1 and answers to previous comments.

l13. 'The anthropogenic and ...' Should that be a new paragraph? It would help to expand on the rationale/concept used to correct for spatio-temporal variations of xCO2 before showing the equations. This paragraph has been removed. Please, refer to new section 2.2.1 and answers to previous comments.

l18. Not clear what the 'above-mentioned elements' are. State clearly what these are (T,S,Si,AOU, xCO2) This paragraph has been removed. Please, refer to new section 2.2.1 and answers to previous comments.

l18. Spell out 'Multiple Linear Regression (MLR). Done.

l18-20. Please refer to new section 2.2.1. It is not clear from this sentence what is being done. This whole section is quite cryptic and needs to be explained more clearly. Are bottle data first estimated using MLR and then averaged into region, layers and years or is the MLR performed on averaged data? The former makes more sense, but it is not clear from the text, especially that on p3011, l1, it says 'of the corresponding pH average', suggesting the MLR is performed on a single number (i.e the average). One cannot do a regression against a single number, so this is very confusing. This is not what was done. Please, refer to the new section 2.2.1. Also, the rationale for equation (1), to use a partial set of linear regression coefficients (ai) and apply those to a difference between averaged measured and climatological properties, is not at all clear initially. Explain how this is related to pH. A formal derivation would be helpful not only for the reader to understand the rationale but also in trying to assess the assumptions behind the calculation.

****p3011**

l4. How good are the regression results? All details are given in Table 3 What sort of residual patterns does this calculation result in? Are the Xi values used in the regression basin/layer averages, one for each cruise, such that the regression is done n layer/basin averaged values across all cruises? Please, refer to the new section 2.2.1. 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).

l12-18. The conceptual connection between equation (1) and (2) is not very clear so the explanation given in this paragraph and the effect of removing this term is not easy to evaluate. Please, see the answer to the previous comment and new section 2.2.1. Perhaps it would be possible for the reader to evaluate this point if the amount of variance explained by each variable was given in Table 2, or maybe by showing a step-by-step reconstruction of the signal by adding each element of the MLR one at the time, highlighting the part of the signal that is omitted when keeping this term out of the reconstruction.

l19. How can seasonal detrending be possible if one uses, as l6 seems to suggest, 'averages of the year' in equation (2)? 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, see the answer to previous comments and new section 2.2.1.

l25. The pH corrections calculated from equation (2) are of order 10^-3. This is smaller or similar to the analytical precision and smaller than the errors coming from rescaling the pH scales (0.01 units, p3007, l24). In that case, why bother with this calculation on equation (1) and (2)? Should one conclude that natural variability of pH is small? Is that ΔpHc correction an estimate of natural variability? Would the results be different if that correction was not applied? Some discussion of the effect of that correction and an indication of its geographical pattern along the section would help, maybe a figure also? Please, see new Table 2 (former supplementary tables) and answers to previous comments. 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.

****p3012**

l5. 'The residual correlation'. What is this? Is that the between residuals or something different? This has been deleted since it des not make sense in the new version of section 2.2.1, since the normalization has nothing to do with separating the anthropogenic and natural pH components of pH variability.

3. Resutls

l11. Are this sections in Fig 2 showing pHc or pHc*? They show pH_c (denoted as pH_{SWS25} on the new version of the manuscript) Also make that clear in the Figure caption. Done.

l22. change 'at expenses' to 'at the expense' This sentence has been deleted in the revised version.

****p3013**

l3-4. Not sure what the point of this sentence is ('the dilution of these two ... of the uNADW') beside a restatement of uNADW is a mixture of mostly these two water masses? This sentence has been deleted in the revised version.

l9. Remove 'It must be noticed that in this study the'. Start sentence with 'lNADW...' This sentence has been deleted in the revised version.

l18. Remove 'Later, then,' start with 'The high...' This sentence has been deleted in the revised version.

l26 Remove 'and Supplement' This sentence has been deleted in the revised version.

****p3014**

l2. Some errors are provided for the acidification rates. How are these errors calculated? Do they take into account the errors around each average pH value? Please give a description of how these errors are calculated. Done. The following sentence is introduced at the beginning of the third paragraph in Section 3, right after introducing Fig. 3 (see answer to the next comment): "*The evolution of the average $pH_{SWS25\text{-}BA}$ 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.*".

l5. 'Any of the former...' What are the former? SAIW, SPMW and LSW? This whole paragraph has been rewritten: "*The evolution of the average $pH_{SWS25\text{-}BA}$ 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 ($-0.0019\pm0.0001\ yr^{-1}$) and the uLSW ($-0.0017\pm0.00004\ yr^{-1}$) (both in the Irminger basin), and the SPMW ($-0.0012\pm0.0002\ yr^{-1}$) in the Iceland basin. The $pH_{SWS25\text{-}BA}$ of cLSW in the Iceland basin presents a remarkable average decrease of $-0.0016\pm0.0002\ yr^{-1}$, unlike in the Irminger and ENA basins (-0.00089 ± 0.00004 and $-0.0008\pm0.0001\ yr^{-1}$, respectively). The layer of uNADW shows decreasing $pH_{SWS25\text{-}BA}$ vs. time trends from the Irminger ($-0.0010\pm0.0001\ yr^{-1}$) to the Iceland basin ($-0.0008\pm0.0002\ yr^{-1}$) due to the influence of ISOW and to the mixing with LSW. Overall, the lNADW and uNADW 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: $0.0002\pm0.0002\ yr^{-1}$ ($R^2=0.15$; p-value = 0.57) and $-0.0003\pm0.0001\ yr^{-1}$ ($R^2=0.28$; p-value = 0.47) for lNADW and uNADW, respectively. The MW in the ENA basin showed a moderate acidification rate ($-0.0006\pm0.0001\ yr^{-1}$) due to its known capacity for C_{ant} drawdown by entrainment from surface layers (Ríos et al., 2001; Álvarez et al., 2005).*"

l7. Dore et al. 2009 is for the North Pacific. Is there any reason to expect different values in the North Atlantic? Differences in Revelle Factor? As commented above, this paragraph has been modified, and the reference to Dore et al. 2009 removed.

l17. Replace 'convection' by 'ventilation', unless you mean convection only and exclude any other ventilation process. '...the further southward...' Rewrite sentence. The sentence has been deleted in the revised version.

l17 Revelle Factor is mentioned earlier, introduce acronym on first mention. It is no longer mentioned. This sentence has been deleted in the revised version.

l26. Show lysocline on Figure 2. It would also be good to show the chosen isopycnals on Fig 2. The new version of Fig. 2 includes the isopycnals shown in Fig. 1b to facilitate the visual follow up of pH evolution on the selected water masses.

****3015**

l2. 'were estimated in' change to 'were estimated to be'. Done. Please notice that this paragraph has been moved to the end of the discussion section, right before Section 5.

4. Discussion

l7. Briefly explain why inversions can occur. That is what was explained during the rest of that paragraph. However, this paragraph

l11. 'at the expense of' This part has been removed.

l11. 'which was the first case...' explain the case of what. Probably not first case, but first time observed? We did not write “first”. We meant that during the late 90s, during the low NAO period, the production of uLSW was enhanced, unlike (at the expense of) cLSW formation. In any case, the sentence has been removed in the new version.

l18. Suggestion: 'A volumetric census of the Iceland Basin showed that LSW peaked at that time. The volume injected was big enough...' Thanks, but this sentence has been deleted in the revised version.

l20-23. Conclusion not well supported, imprecise or not well explained. Changes in the ventilation rate of water masses and their associated mixing is a 'natural variability' phenomenon (we agree with this first part of the comment) that should have been filtered by the MLR correction applied. The MLR correction (basin normalization) is not aimed at separating the natural and anthropogenic components of pH variability (se answers to previous comments). The only influence on pHc* should then be due to Canth? Since the basin normalization does not separate anthropogenic and natural components, any of the here-considered pHs (pH_{SWS25} or $pH_{SWS25-BA}$ –previously denoted pH_C*) is susceptible to be influenced by C_{ant}, as we argue in various sentences in the discussion section. In the context of the new discussion section, this is how this sentence appears in the new version (penultimate paragraph of the discussion section): “*…The high-NAO enhanced ventilation that occurred towards the mid-late 1980s fostered the fast formation of a massive cLSW vintage (Kieke et al., 2007; Yashayaev et al., 2008). The rapid subduction of this newly formed cLSW meant an injection of C_{ant} from surface to intermediate waters, transporting C_{ant} much faster than via downward diffusion alone, thus causing a faster acidification rate in the cLSW (where organic matter remineralization also contributes significantly to the pH lowering) than in the SPMW, where C_{ant} influence is the main contributor to acidification.”.* This statement about vertical mixing versus lateral mixing/advection seem also a little out of place as this work does not quantify these processes. This needs some explanation. We hope to have cleared this comment in the new manuscript version.

l24. Change 'plausible' to 'possible' This sentence has been deleted in the new version. The way we present the pH projections has changed. Please, refer to the fourth paragraph on the new discussion section to see full modifications. The sentence now begins like this: "*...From our set of $pH_{SWS25\text{-}BA}$ observations we have made projections of future pH levels (Fig. 4)...*".

l27. Is it variability in the ocean circulation that should stay constant (natural variability is mostly driven by changes in the physics and so should have been removed by pHc* -This has nothing to do with the basin normalization. See previous answers) or overall ocean circulation? That seems too restrictive. It is somewhat restrictive and we are aware of it, but we discuss our assumption and its limitations in the text. Please, see answer to comment on **p3016, line 120-22. Please explain. Idem.

****p3016**

l1-7. Style suggestion: 'The SPMW and cLSW are selected for such a projection as they are amongst the water masses that are the most susceptible to human-human induced acidification (Fig 3b). Furthermore, SPMW represents...' Thank you. This is how the sentence is written on the revised version (fourth paragraph on the discussion section): "*...The SPMW and cLSW 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).*".

l8. '... is that a NAO-positive (or negative?) regime prevailed...' 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.

l12. What do you mean by 'not constrained'? We mean that we do not impose any restriction to the evolution of pH. Therefore, we assume that, under an analogous anthropogenic forcing and general circulation conditions as during the observation period, the acidification trends will remain linear in those water masses. The extrapolation is linear, based on the linear trends obtained in Fig. 3. The uncertainty bands are computed statistically from the observation-based points available.

l18. 'these processes' Done. Thanks.

l20-22. Awkward sentence. Rewrite and be more specific, explain more clearly. This part has been removed. This is how the discussion about the "constant general circulation assumption" looks like in the new version (sixth paragraph on the discussion section): "*...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...*".

l24. A decrease in pH levels means an acidification? I'm not sure that's what you mean here.

Correct. We have rewritten this part of the sentence for clarity: "*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).*".

l27. 'obtained' change to 'calculated'? Done. New sentence goes as follows (fourth paragraph on the discussion section): "*...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...*".

l29. Why put Fig S1 as a supplement and not as an integral part of the paper? Almost 50% of the discussion section is dedicated to it. 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.

****p3017**

l1-7 These sentences are very wordy. Simplify. Done: "*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 ppmv, which is consistent with outputs from coupled climate/carbon-cycle models (Caldeira and Wickett, 2005; Orr et al., 2005). In the case of cLSW, 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 ppmv (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.* ".

l5-8. 'Differently...' this sentence not clear. Why compare results to a model here? What are these 0.25 pH units referring to? See answer to previous comment.

l8. Remove 'notorious' and emphasize 'THIS model-based...', unless you can prove all models do that. By the way, why only compare to that model? Done. This particular model has been widely accepted, that is why we chose it as a reference for comparison.

l12. 'for the desired level of accuracy'. Accuracy in what? Circulation strength in the NASPG, general meridional overturning, or just pH? Be specific. This sentence was written awkwardly. We have replaced it by the following (seventh paragraph on the discussion section): "*...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...*".

l21-24. This seems to be an important results of the study. Emphasize it and discuss it more fully. Done. We have included more results and discussed it more thoroughly. See the last three paragraphs of the modified discussion section:

“*The aragonite saturation state is defined as* $\Omega_{\mathrm{arag}} = [\mathrm{Ca}^{2+}][\mathrm{CO}_3^{2-}]/\mathrm{K}'_{\mathrm{sp}}$ *, where square brackets indicate seawater ion concentrations and* $\mathrm{K}'_{\mathrm{sp}}$ *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 cLSW in the Iceland basin for atmospheric* xCO_2 *values of 380 (present day), 500 and 750 ppmv (see insets in Fig. 4). The results suggest that cLSW would actually reach aragonite undersaturation (*$\Omega_{arag} < 1$*) by the time atmospheric* CO_2 *reaches ~550 ppmv and not 900 ppmv, 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 cLSW vintage (Kieke et al., 2007; Yashayaev et al., 2008). The rapid subduction of this newly formed cLSW meant an injection of* C_{ant} *from surface to intermediate waters, transporting* C_{ant} *much faster than via downward diffusion alone, thus causing a faster acidification rate in the cLSW (where organic matter remineralization also contributes significantly to the pH lowering) than in the SPMW, where* C_{ant} *influence is the main contributor to acidification. Depending on the future* CO_2 *emission rates the 550 ppmv threshold at which, according to our projections, cLSW would face aragonite undersaturation, could be trespassed in 2050, or before (Nakicenovic et al., 2000; Caldeira and Wickett, 2005; Feely et al., 2009).*

The data analysis also showed that the aragonite saturation depth (or lysocline = isopleth where $\Omega_{arag} = 1$*) 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).*”.

l25. 'step over the brink of the' replace by 'pass' The sentence has been changed to: “*Depending on the future* CO_2 *emission rates the 550 ppmv threshold at which, according to our projections, cLSW would face aragonite undersaturation, could be trespassed in 2050, or before (Nakicenovic et al., 2000; Caldeira and Wickett, 2005; Feely et al., 2009)*.”.

****p3018**

l2. What is 'extensive North Atlantic vertical mixing'? We meant strong convection activity. Also, it was stated earlier that vertical mixing was not important. Where? How can it be important for Canth but not for pH? It is important for both variables in the regions where C_{ant} uptake is enhanced by water mass formation processes that are favoured by convection (like the case of cLSW). This way, important loads of C_{ant} are taken up by the ocean and that translates into a larger pH drop. The penultimate paragraph on the discussion section now includes the following: “…*The high-NAO enhanced ventilation that occurred towards the mid-late 1980s fostered the fast formation of a massive cLSW vintage (Kieke et al., 2007; Yashayaev et al., 2008). The rapid subduction of this newly formed cLSW meant an injection of* C_{ant} *from surface to intermediate waters, transporting* C_{ant} *much faster than via downward diffusion alone, thus causing a faster acidification rate in the cLSW (where organic matter remineralization also contributes significantly to the pH lowering) than in the SPMW, where* C_{ant} *influence is the main contributor to acidification.*” The abstract says vertical mixing not important. We are sorry, but we cannot find where in the abstract we stated that. It actually sounds contradictory.

**p3019

5. Discussion

l10. It seems hard to believe that accuracy limits of 0.0001 pH units change per year can be achieved given the measurement accuracy of 0.002 and the problem of pH scale. Please explain in your methods section how you compute errors throughout the paper. Done, and also at the beginning of the third paragraph in Section 3, right after introducing Fig. 3 (see previous answer to comment in line 2, page 3014).

Observed acidification trends in North Atlantic water masses

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Abstract

The lack of observational pH data has made difficult assessing recent rates of ocean acidification, particularly in the high latitudes. Here we present a time series that spans over 27 years (1981-2008) of high-quality carbon system measurements in the North Atlantic that comprise fourteen cruises and cover the important water mass formation areas of the Irminger and Iceland basins. We provide direct quantification of acidification rates in upper and intermediate North Atlantic waters. The highest rates were associated with surface waters and with Labrador Seawater (LSW). The Subarctic Intermediate and Subpolar Mode waters (SAIW and SPMW) showed acidification rates of -0.0019±0.0001 and -0.0012±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 < σ_θ < 27.76 kgm^{-3}; between 27.76 < σ_θ < 27.81 kgm^{-3}, respectively. The North Atlantic Deep Water (NADW, which includes the ISOW contributions) is delimited by 27.81 < σ_θ < 27.88 kg m^{-3}, and the Denmark Strait Overflow Water (DSOW) by σ_θ >27.88 kg m^{-3} (Fig. 1b).

2.2.1 Basin normalization of average pH_{SWS25}

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

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

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 $pH_{SWS25-BA}$ 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 $pH_{SWS25-BA}$ 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 $pH_{SWS25-BA}$ 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 $pH_{SWS25-BA}$ 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 $pH_{SWS25-BA}$ 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 $pH_{SWS25-BA}$ 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 $pH_{SWS25-BA}$ 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 $\left(\partial \mathrm{pH} / \partial t\right)_{\mathrm{ANT}} = \left(\partial \mathrm{C}_{\mathrm{ANT}} / \partial t\right)\left(\partial \mathrm{pH} / \partial \mathrm{C}_{\mathrm{T}}\right)_{(\mathrm{S}, \mathrm{A}_{\mathrm{T}})}$, where $\left(\partial \mathrm{pH} / \partial t\right)_{\mathrm{ANT}}$ is the expected variation over time of human-induced pH (due to C_{ant}); $\left(\partial \mathrm{C}_{\mathrm{ANT}} / \partial t\right)$ is the corresponding C_{ant} storage rate (from Pérez et al., 2010); and $\left(\partial \mathrm{pH} / \partial \mathrm{C}_{\mathrm{T}}\right)_{(\mathrm{S}, \mathrm{A}_{\mathrm{T}})}$ 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 ($\Omega_{arag} <1$) 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 $\mu mol\cdot kg^{-1}$.

(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 $\mu mol\cdot kg^{-1}$.

Table 2a. Irminger Basin

Year	Salinity	θ (ºC)	AOU (μmol·kg^{-1})	Si(OH)$_4$ (μmol·kg^{-1})	pH $_{SWS25}$	ΔpH $_{SWS25-BA}$	pH $_{SWS25-BA}$
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

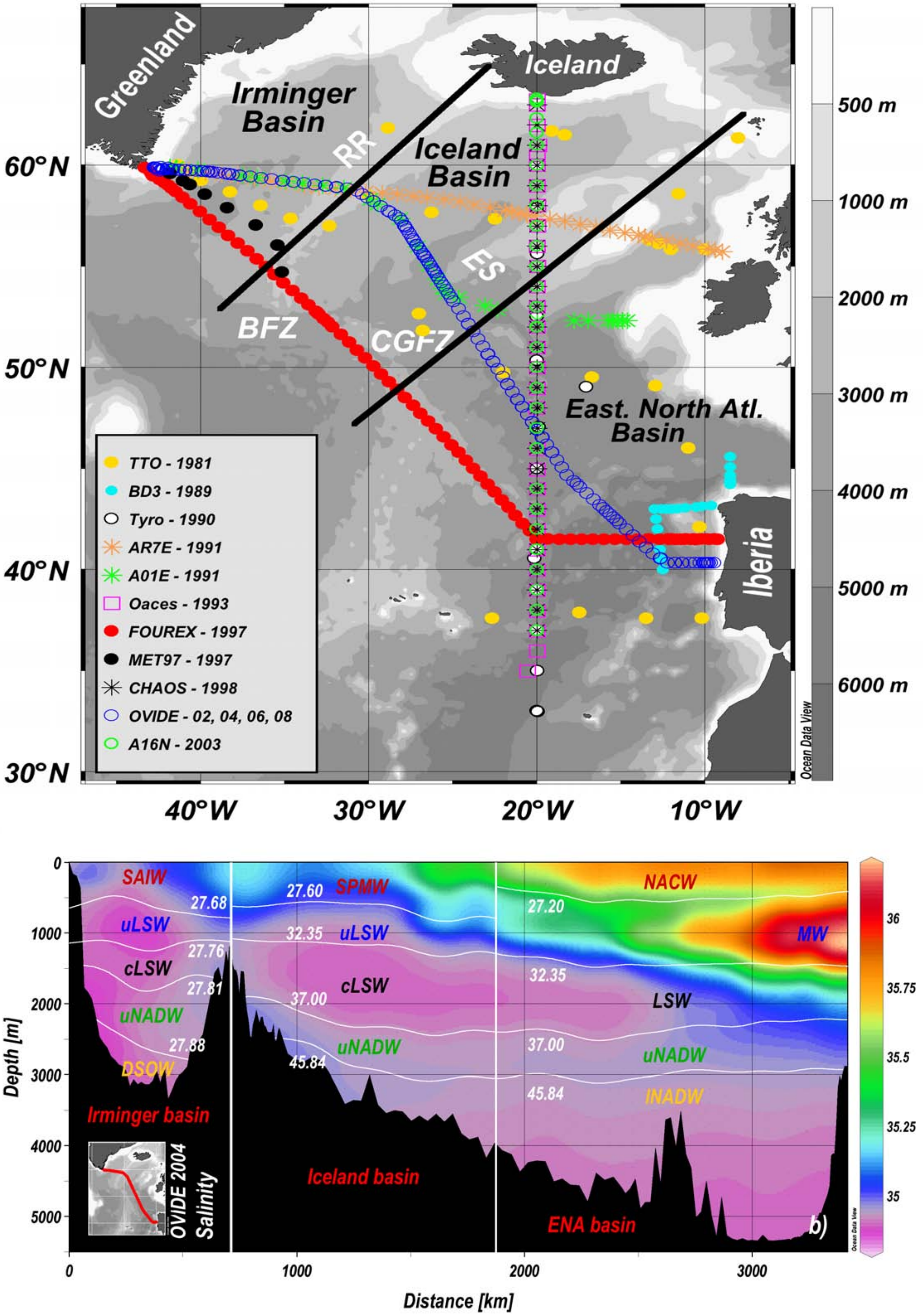
Year	Salinity	θ (ºC)	AOU (µmol·kg^{-1})	Si(OH)$_4$ (µmol·kg^{-1})	pH$_{SWS25}$	ΔpH $_{SWS25-BA}$	pH $_{SWS25-BA}$
SPMW (σ_0 <27.60 kg m^{-3})							
1981	35.183 ± 0.001	8.242 ± 0.003	28.2 ± 0.1	6.89 ± 0.04	7.814 ± 0.001	-0.008 ± 0.005	7.806 ± 0.005
1991	35.109 ± 0.001	7.030 ± 0.003	22.9 ± 0.2	7.73 ± 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

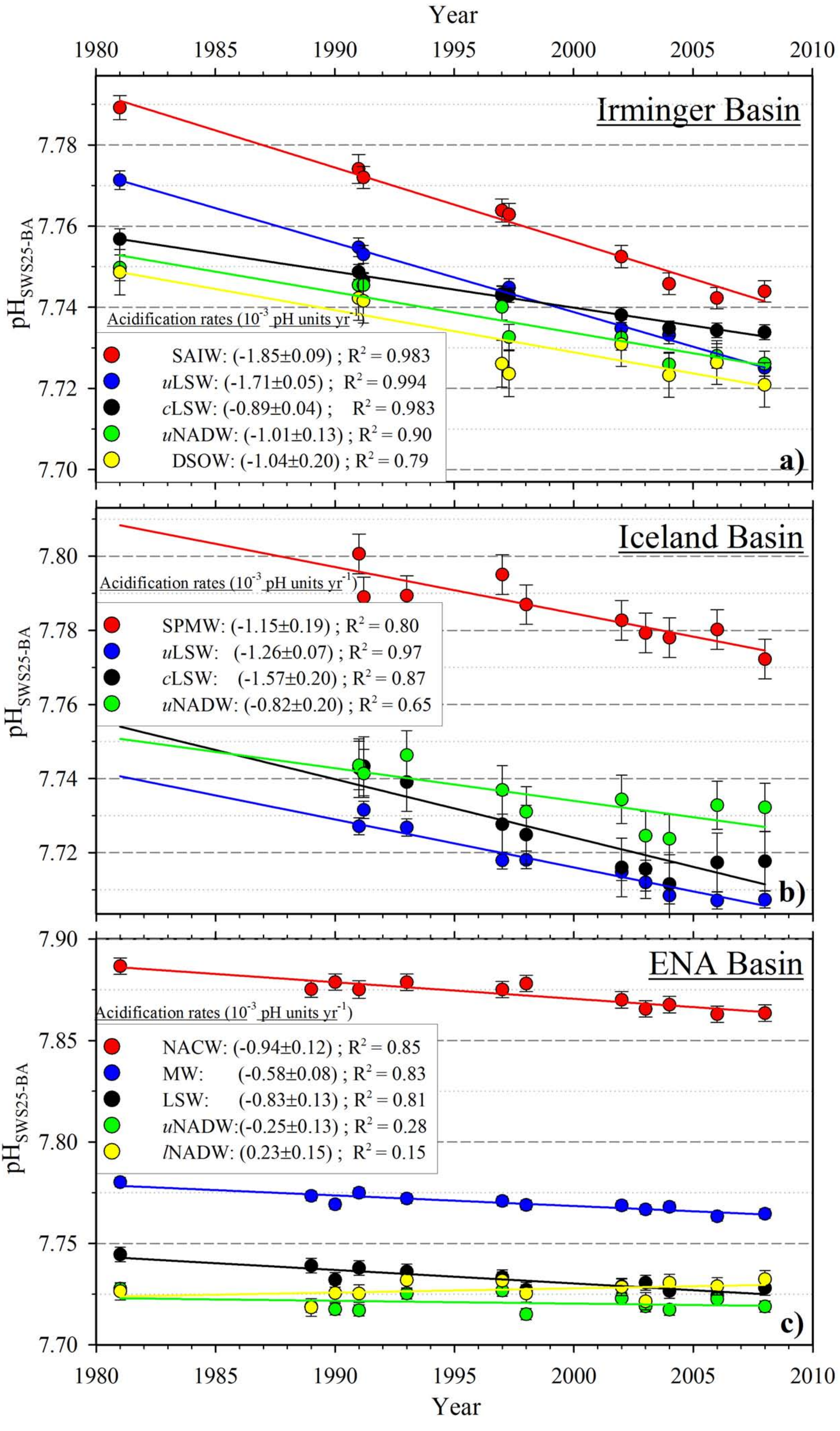
Table 3.

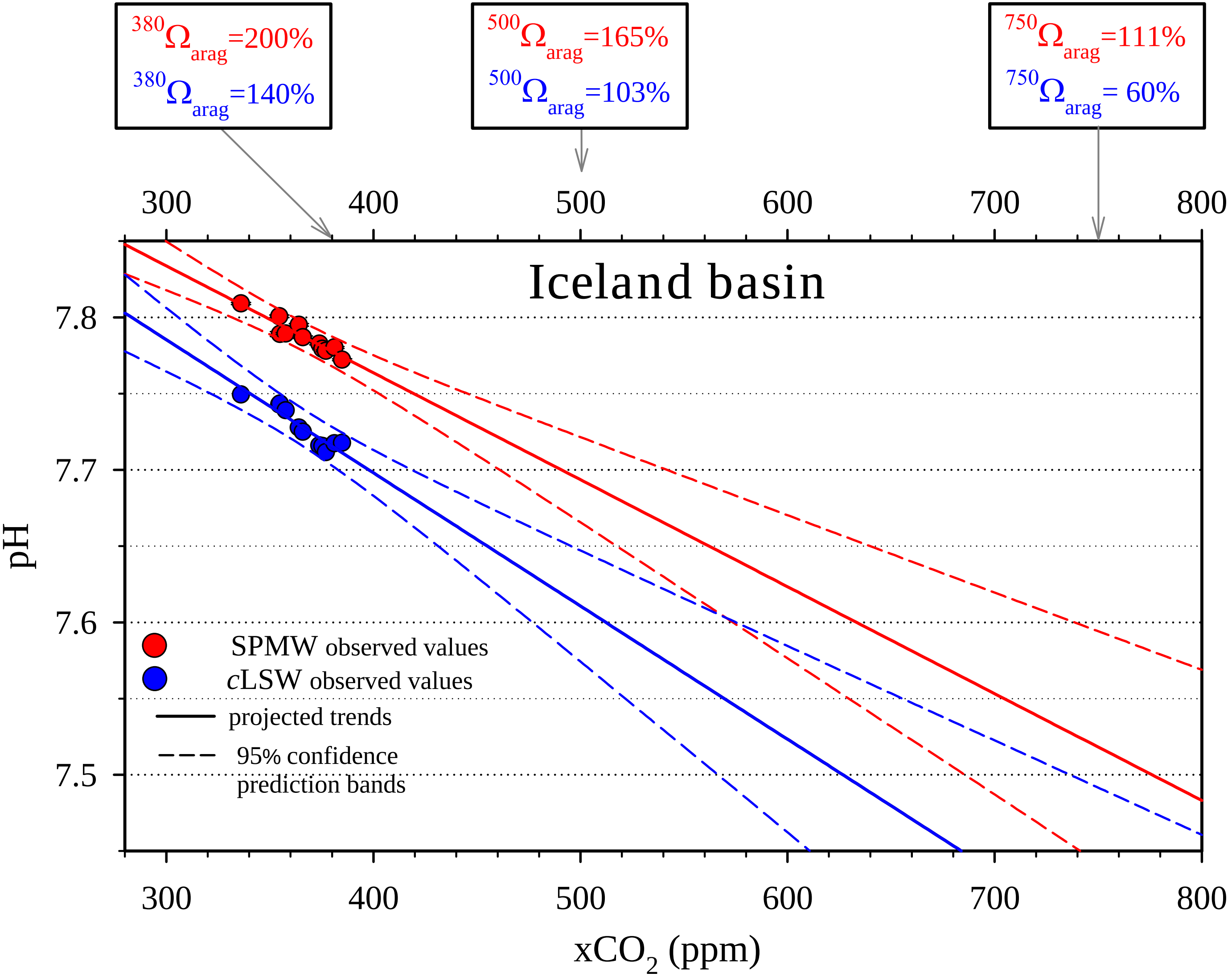
Water Mass	R^2	Estimated error	a_1 (xCO_2 ; ppm^{-1})	a_2 ($Si(OH)_4$; $kg \cdot \mu mol^{-1}$)	a_3 (AOU ; $kg \cdot \mu mol^{-1}$)	a_4 (θ ; $°C^{-1}$)	a_5 (S)
Irminger Basin							
SAIW	0.97	0.003	-1.02 ± 0.08	-15 ± 2	n.s	n.s	0.18 ±0.03
*u*LSW	0.99	0.002	-0.95 ± 0.04	-11 ± 1	n.s	30 ± 10	0.67 ±0.08.
*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
27.68
27.60
27.20
uLSW
32.35
uLSW
MW
27.76
cLSW
27.81
cLSW
32.35
37.00
LSW
uNADW
27.88
uNADW
37.00
uNADW
DSOW
45.84
45.84
lNADW
Irminger basin
Iceland basin
ENA basin
OVIDE 2004 Salinity
b)
Depth [m]
0
1000
2000
3000
4000
5000
Distance [km]
0
1000
2000
3000
36
35.75
35.5
35.25
35
Ocean Data View


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


Year
1980
1985
1990
1995
2000
2005
2010
Irminger Basin
pH$_{SWS25\text{-}BA}$
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$_{SWS25\text{-}BA}$
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$_{SWS25\text{-}BA}$
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
pH
7.8
7.7
7.6
7.5
● SPMW observed values
● *c*LSW observed values
projected trends
95% confidence prediction bands
300
400
500
600
700
800
xCO_2 (ppm)