

REVIEW

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. *Biogeosciences Discuss.* (bg-2012-83) 9:3003-3030

GENERAL COMMENTS

Vazquez-Rodriguez 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 previous 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 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. 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) 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.

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. 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. 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. Section 2.1 is thus also very similar to paragraphs in Sec 2 in Perez et al. 2010.
- This paper also presents very related data, that is the increase in Canth in the same layers treated in this paper.
- Figure 1 is also identical to Perez et al. 2010, with the addition of OVIDE2008.
- Sec 2.2.2 is also very similar to Perez et al, 2010, section A2.

SCIENTIFIC COMMENTS

Section 2.2.2 “Normalization and averaging of pH” is particularly confusing. This is clearer in Perez et al. 2010. This section describes a methodology to remove the effect of natural variability from the total signal. 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.

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.

Overall, the manuscript would also benefit from a description of how errors are treated and a discussion of these errors 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.

The authors should also provide a general discussion of the Δp_{Hc} 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 Δp_{Hc} elements is necessary.

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). 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. What do the other layers show (at least show the acidification rate in Table 2 for all layers)? 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.

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 p_{Hc} ? 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. 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? 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?

TECHNICAL COMMENTS:

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**

- 112-13 Why 'surprisingly'?
- 114 'unprecedented' – since these are the first measurements, it's hard to make any statement like that.
- 118. linear
- 120. ...by the time atmospheric CO2 concentrations double the present ones. Does this statement depend on emission rates and ventilation rates?

1. Introduction:

- 122. ...is well known and researched. Perhaps just say 'is known'
- 123. remove ',' before but
- 123. 'its' as written would refer to 'the chemistry'. Restructure sentence.
- 126. 'quenched'. word choice.

****p3005**

- 11. 'hampering'. word choice.
- 14. remove 'the so-called'
- 15. sea-surface's should be sea-surface
- 15. 'on' pH, should be 'in' pH

- 15-6. '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.
- 19-10. ...,and it is the onset... maybe best to replace by 'is thought to be the onset...'
111. 'Ocean acidification has a medley of juxtaposed...' word choice/style. Rewrite sentence.
- 120-21. '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.
123. '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? What about the Southern Ocean?
124. 'The negative feedback...' This sentence does not seem to fit in this paragraph.
128. 'There are relatively few spots...' It would be informative to give a list of where this is possible.

****p3006**

- 15-9. *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.
16. '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.
17. '...high-quality, NASPG-covering carbon...' replace by 'high-quality carbon system data covering the NASPG between ...'

2. Dataset and methodology

2.1 Dataset

112. 'the relatively recent introduction' just say 'the introduction'
113. 'allowed making fast and yet very accurate' just say 'allowed for fast and accurate'
114. 'filling the need of improving and enlarging...synthetic data get tested'. Style/english, rewrite sentence. What are 'synthetic data'? 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.
118. 'spans over 27 years', just say 'spans 27 years'
121. 'have been established' replace by 'are defined by the main...'
125. rewrite 'Eastern North Atlantic (ENA) basin'

****p3007**

11. 'Cruise data can be accessed', remove 'used here'
15. 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).'
17. 'only bottle data of the inorganic carbon system WERE used'.
18. '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.
- 112-17. 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).'
120. '...constants for HF and HSO₄⁻.' Indicate in Table 1 where these calculations were necessary.
- 123-24. '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?
126. '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.
- 126 to p3008, 12. This sentence does not belong this paragraph. This paragraph is about how Alk and DIC were measured.

****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.

****p3009**

2.2 pH data analysis

2.2.1 Water mass approach

13-4. Reference needed for that statement, linking the strength of anthropogenic CO₂ uptake with the process of convection.

15. Please explain how convection changes carbon chemistry?

19-10. Say what is being followed exactly (e.g. alkalinity, etc.) instead of saying 'carbon system parameters'

112. '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. *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. 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.*

2.2.2 Normalization and averaging of pH data

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.

122-23. Were climatological averages calculated on isopycnals?

124-25. Instead of 'per water mass', it would be best to say 'between isopycnal layers and per year'.

125. Is the fundamental reason for doing the isopycnal and annual binning only because of convenience in plotting? What effect does this averaging have on the final results. Would using different layers change the analysis? Is there a significant temporal summer bias in the distribution of the data?

126-27. 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.

****p3010**

11-3. 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.

110. I'm not sure what 'ventilation ... can be traced' means. Should it be 'ventilation pathways ... can be traced'? or can ventilation rates be calculated?

110. Given the different interpretation of ventilation, the term 'accurately' is a very subjective statement.

112. 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? It is not immediately clear that this is the case.

113. '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.

118. Not clear what the 'above-mentioned elements' are. State clearly what these are (T,S,Si,AOU, xCO₂)

118. Spell out 'Multiple Linear Regression (MLR)'.
118-20. 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, 11, 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. Also, the rationale for equation (1), to use a partial set of linear regression coefficients (a_i) 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**

14. How good are the regression results? What sort of residual patterns does this calculation result in? Are the X_i values used in the regression basin/layer averages, one for each cruise, such that the regression is done on layer/basin averaged values across all cruises?

112-18. 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. 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.

119. How can seasonal detrending be possible if one uses, as 16 seems to suggest, 'averages of the year' in equation (2)?

125. 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, 124). 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 $\Delta p\text{H}_c$ 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?

****p3012**

15. 'The residual correlation'. What is this? Is that the between residuals or something different?

3. Results

111. Are these sections in Fig 2 showing $p\text{H}_c$ or $p\text{H}_c^*$? Also make that clear in the Figure caption.

122. change 'at expenses' to 'at the expense'

****p3013**

13-4. 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?

19. Remove 'It must be noticed that in this study the'. Start sentence with 'INADW...'

118. Remove 'Later, then,' start with 'The high...'

126. Remove 'and Supplement'

****p3014**

12. 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.

15. 'Any of the former...' What are the former? SAIW, SPMW and LSW?

17. 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?

117. Replace 'convection' by 'ventilation', unless you mean convection only and exclude any other ventilation process. '...the further southward...' Rewrite sentence.

117. Revelle Factor is mentioned earlier, introduce acronym on first mention.

126. Show lysocline on Figure 2. It would also be good to show the chosen isopycnals on Fig 2.

****3015**

12. 'were estimated in' change to 'were estimated to be'

4. Discussion

17. Briefly explain why inversions can occur.

111. 'at the expense of'

111. 'which was the first case...' explain the case of what. Probably not first case, but first time observed?

118. Suggestion: 'A volumetric census of the Iceland Basin showed that LSW peaked at that time. The volume injected was big enough...'

120-23. 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 that should have been filtered by the MLR correction applied. The only influence on $p\text{H}_c^*$ should then be due to Canth? 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.

124. Change 'plausible' to 'possible'

127. 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*) or overall ocean circulation? That seems too restrictive. Please explain.

****p3016**

11-7. 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-induced acidification (Fig 3b). Furthermore, SPMW represents...'

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

112. What do you mean by 'not constrained'?

118. 'these processes'

120-22. Awkward sentence. Rewrite and be more specific, explain more clearly.

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

127. 'obtained' change to 'calculated'?

129. 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.

****p3017**

11-7. These sentences are very wordy. Simplify.

15-8. 'Differently...' this sentence not clear. Why compare results to a model here? What are these 0.25 pH units referring to?

18. Remove 'notorious' and emphasize 'THIS model-based...', unless you can prove all models do that. By the way, why only compare to that model?

112. 'for the desired level of accuracy'. Accuracy in what? Circulation strength in the NASPG, general meridional overturning, or just pH? Be specific.

121-24. This seems to be an important result of the study. Emphasize it and discuss it more fully.

125. 'step over the brink of the' replace by 'pass'

****p3018**

12. What is 'extensive North Atlantic vertical mixing'? Also, it was stated earlier that vertical mixing was not important. How can it be important for Canth but not for pH? The abstract says vertical mixing not important.

****p3019**

5. Discussion

110. 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.