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

Anonymous Referee #2

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In this paper the authors use a large collection of data for the subpolar North Atlantic (SPNA) in order to quantify the change in interior ocean pH over about 3 decades. The SPNA is well suited for this as large amounts of anthropogenic carbon (Cant) is taken up and stored in this region, and this region is relatively well sampled in comparison to other ocean regions. The SPNA is also a very active area with significant changes in water mass composition and properties over the last decades and the observational record (probably for much longer than that, but without observations to verify this). The authors show trends of observed pH trends in the SPNA over 3 decades, and attempt to project these trends linearly into the next 50 or so years. The theme of the manuscript is well suited for publication in BG, but both the methods and the result/discussion sections is in the need of significant improvements.

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Main concerns:

The methods section of this manuscript needs considerable improvements. I do not understand why the authors only use density layers that vary between basins to determine water masses. The authors have access to several other parameters that can help distinguish different water masses with similar densities. This can potentially lead to problems with some water masses such as Mediterranean Water. A more serious problem is probably the temporal variability aspect of this problem. Changes in water mass properties in the SPNA are well documented, and the authors refer to some of these studies. The authors write: “The main factors that modulate the natural variability of ocean pH on decadal timescales need to be removed from observations in order to isolate and evaluate the anthropogenic forcing and its effects in ocean acidification”, and then sets out to remove the “natural variability”. It is not clear to me why one should take out decadal variability for a study concerned with decadal changes; it seems to defeat the purpose of the study. It is also not clear that the variability they apparently remove is natural. The authors present no evidence for that. If the variability is a result of anthropogenic changes effecting circulation, temperature, oxygen etc. would it not be a very bad idea to remove that signal? The section describing the normalization and averaging of pH data is very difficult to understand. I have tried hard, and I think I know what the authors did, but it is not clear to me why they did it this particular way; or why they did it at all, for that matter. It occurs to me as a strange way of normalizing the pH values. It is not clear to me that the factors (a) in equation 1 and 2 can be directly compared as the authors do, since equation 2 has one more term. The authors state that the Delta-pH_c term is spatially and seasonally detrended. Firstly, is this not a normalization to climatological conditions for a water mass, rather than a spatial normalization? Secondly, how does the seasonal signal transports to the interior ocean? Is this even worth doing, except for the surface waters? Also, coming back to my previous concerns, why “reference to average climatological conditions” at all? Looking at the values in tables S1 to S3 there seems to be a clear decreasing trend for most water masses without any normalization to climatological conditions. Why not report

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on the trend of the averaged observed pH for each water mass? I think that is the very least that should be done in order for the reader to understand how large influence the “normalization” process has on the trends. The ΔpH_c term is not reported on in any of the tables, which I think it should be (if at all used). Further the comment that the ΔpH_c term is in the order of $\sim 10^{-3}$, and therefore not so important, might not be true. You are reporting of trends in pH in that order of magnitude. In summary, a lot of confusing calculations are presented to come up with an adjustment (ΔpH_c) that, according to the authors, has “a very small weight in pH_c ” and to me seems to be poorly justified scientifically in the first place.

In the Result section I found it interesting that cLSW has experienced large acidification rates in spite of low ventilation the last decade or so. It would be interesting to read a few lines of thought on why that is. It seems to suggest that the “acidification” due to respiration is more important than the uptake of C_{ant} from the surface. In many instances these two effects are confused in the manuscript, and in the end I wonder if a fast ventilated water mass should be more affected by acidification, or a water mass whose ventilation rate has decreased. For instance, in the beginning of the discussion the authors state that “pH normally decreases with depth” (presumable due to respiration of organic matter), and a few lines later they state that “surface water with lower average pH” is injected to depth explaining a mid-depth minima in pH. Similarly, on page 3016 the authors state “The hampered ventilation from increased surface ocean stratification is expected to bring about a decrease in dissolved oxygen concentrations and pH levels, amongst other things because C_{ant} would not be as effectively transported toward the ocean interior via deep convection and water mass formation processes (Perez et al., 2010)”. Why should pH decrease if LESS C_{ant} is injected? I don’t question the statement, but the driver of the change has to something else, such as respiration.

Prediction of future pH values: Since such a big part of the discussion is devoted to this subject, why is the figure contained in the supplementary material? Is a decrease

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in pH for cLSW of 0.45 units consistent with the thermodynamics of the carbonate system for a pCO₂ of 775 ppm? Can it be that the high trend for cLSW “acidification” is a result of low ventilation recently, and that if the cLSW becomes better ventilated in the future, waters with higher pH will dominate this water mass, so that your linear trends are wrong? It seems to me that the high level of pH decrease in cLSW is due to respiration, which can change if the ventilation increases again.

Minor / technical comments:

• Page 3004, line 26: What is excess anthropogenic CO₂. When referring to a percentage, make very sure if you talk about fossil fuel emissions only, or if you include land use change, and also for which time frame you are presenting these numbers. They are all different.

• Page 3007, line 17. Do the authors mean “higher” precision rather than “lower”?

• Page 3008, line 18: What is “timely date”?

• The normalization of alkalinity on page 3008 assumes a zero intercept, which has been shown by (Friis et al., 2003) to be flawed. I suggest changing this.

• Page 3009, line 3: Please avoid words like “exceptionally”. The authors seem to forget the southern ocean is the region where most of the Cant is taken up.

• Page 3010, line 10: AOU does not “accurately” trace ventilation. Strictly AOU traces respiration, and an assumption of constant respiration has to be made to convert AOU into ventilation.

• Page 3011, line 8. “Selected meteorological stations”. State which ones, and why you not use the well-known average CO₂ concentration for the northern hemisphere.

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

• Page 3012, line 15: “more acidic”? The pH is about 7.7 in this water mass. This is well above neutral pH. More correct would be “less basic”. This applies to a number of instances in this paper, for instance a few lines down on the same page; “NADW is natural acidic” – that is simply not true.

• Figure 2. Is it necessary to present pH sections for all the OVIDE lines? You are

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hard pressed to visually see any differences, and you still don't know if differences you might see (such as in the deep Irminger Basin are due to variability in water masses rather than acidification. The difference between 1991 and 2008 is striking though. [â€” Page 3014, line 5](#): The sentence starting with “Any of. . .” is unclear. What is the “maximum acidification rates achievable during 1981 to 2008”. [â€” Page 3014, line 8](#): Iberian basin? [â€” Figure s1](#): Normally is the Omega value not given as percent. [â€” Table 1](#): Which version of the TTO data is used? There is an updated version of the TTO data available, see (Tanhua and Wallace, 2005). [â€” Figure 3](#). In a recent publication by one of the co-authors of this study, the trend (in that case of Cant) was better fitted vs. the atmospheric perturbation of CO2 than vs. time. Why is that not done in this paper? It would at least provide some confidence check on the results, i.e. if the trends extrapolated to zero atmospheric perturbation is very different from a ΔpH of zero, there might be a problem.

References:

Friis, K., Kortzinger, A., and Wallace, D. W. R.: The salinity normalization of marine inorganic carbon chemistry data, *Geophys. Res. Letters*, 30, -, 2003.

Tanhua, T., and Wallace, D. W. R.: Consistency of TTO-NAS Inorganic Carbon Data with modern measurements, *Geophys. Res. Letters*, 32, L14618, 2005.

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