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Interactive comment on “Rapid acidification of mode and intermediate waters in the southwest Atlantic Ocean” by L. A. Salt et al.

Anonymous Referee #1

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Review of Salt et al. " Rapid acidification of mode an intermediate waters in the southwest Atlantic Ocean".

This paper is comparing carbon and related biogeochemical variables along a repeat section in the southwest Atlantic Ocean that was occupied in 1994 and repeated in 2012. The paper focuses on the uptake of anthropogenic carbon, the decrease in pH, and on a discussion on buffer factors in the various water masses and a quantification of the sensitivity to increasing DIC concentrations in the ocean. The paper is generally well written and scientifically relevant questions are being addressed. The manuscript deserves to be published in BG but some deficits needs to be addressed; most seriously is some probably erroneous calculations of one of the buffer factors. Another deficit is the neglect to utilize data from this section occupied in other years

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(2002, 2003 and 2013 by the Spanish ship Hesperides). In the discussion section the authors argues that the eMLR results is reliable in the surface waters. This is first of all surprising since the eMLR results indicates zero carbon uptake in the tropical North Atlantic, and secondly it is a different view from most previous studies that used eMLR. On pages 6771-2 the calculated (from AT and DIC) pCO₂ between the two repeats is presented, with a difference in the DeltapCO₂ (i.e. the ocean / atm. gradient) of 11 ppm. This is a large difference in the dis-equilibrium, and not “relatively consistent” as the authors suggest. However, and most importantly, the authors are trying to deduce sensible differences in the air-sea disequilibrium from the difference between two cruises in an area of significant seasonal variability (about +/- 20 ppm, [Takahashi et al., 2009]). The authors admit to “changes in temperature or other physical processes may exert controls undetectable to our analysis”, and to “variations in chemical stoichiometry which could not be accounted for” with regard to eMLR results in surface waters. Based on the evidence presented in the manuscript, the consistency between the eMLR data and “what can be expected from increase in pCO₂” is coincidental, with large areas where there is no such consistency. In the current version of the ms. I see no evidence for eMLR being any better than the expected DIC increase calculated from TA, sal etc. and the atmospheric increase in pCO₂. To be able to state that “the surface ocean uptake of CO₂ is less/more than expected” regular sampling over the year will be needed. I suggest to modify the discussion of the validity of the eMLR analysis in the surface waters. For the discussion on buffer-factors it would be very helpful to: 1) have the density intervals separating the water masses marked on the sections in Figure 5, and 2) a table with the values of the buffer factors for each water mass. Maybe this is a personal preference, but in the discussion on buffer capacity of various water masses, I think the discussion is incomplete without including the Revelle factor. The discussion on buffer factor will have to be modified once the correct omegaDIC values have been calculated (if in error, which I think they are). Specific comments: Page 6756, line 20: Consider removing the word “current” in light of the text in the next sentence. Page 6757, line 10: This statement is probably not true for the global ocean.

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For instance see paper by Yool et al. [2010]. Page 6758, line 6: If the decrease is -0.1 unit, does that mean that pH increased? Please reformulate. Page 6760, line 2: I do not think the expression “no longer present” is correct. Maybe it would be better to say “is unstable”, or “will dissolve”. There are also kinetics to dissolution of sinking particles that needs to be considered. Section 2.1: It is common practice, and a requirement, that the data used for a publication is publically available for other scientists to reproduce the results. Where are the Dutch 2011 data publically available? If the date are not publically available it would be appropriate not to publish this paper in BG. Section 2.1: The 1994 data have been subject to so called secondary quality control in order to identify any systematic biases in the data (not only the carbonate system variables). Is this the case for the Dutch data as well? Biases in auxiliary variables can bias the eMLR analysis. Page 6763, line 23: It is mentioned that pressure is used in the regression. Why is P not in equation 2? Please correct equation and discussion below eq 2. Page 6764, equation 5: This is most likely in error. Due to editorial errors in the paper by Egleston et al. (2010) this equation is not correct. This is unfortunate, and not easy to spot by the authors. It was noted for the first time in a recent paper by [Álvarez et al., 2014] Please see either the thesis of Egleston or the paper by Álvarez et al. [2014] for the correct expression. This will obviously have consequences for the discussion in the paper that needs to be correspondingly modified. Figure 3: The font-size of the text in these panels is too small to read. Please modify. For the discussion it would be very useful to include iso-lines of density corresponding to the water mass divisions on these plots. Same is valid for the other sections in other figures, e.g. Figs 4 and 5. Page 6765, line 16: Why “below 1000 meter”? The discussion is about AABW (below 4500 m), or not? It would be useful to have the characteristics of the water masses in a table. Page 6767, line 21: The discussion on warm surface water is not correct in this context; high temperatures as in the tropical Atlantic leads to high buffering capacity and potentially high Cant concentrations. That the eMLR shows zero Cant concentrations at the surface must have other reasons. Page 6768, line 22: This is inconsistent with the analysis above, see point made above. Either you use

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the eMLR analysis and discuss temporal variability (using more than the 2 repeats you report on) both on seasonal, annual and decadal time-scales, or you accept that the eMLR on surface waters is unreliable and base your calculations solely on expected changes of surface water based on atmospheric CO₂ change. Section 4.2: The same discussion about close to surface waters does apply to this section as well. Page 6770, line 15: An acidification rate of -0.0005 /y means that the pH value increases. Please exchange “acidification” to Delta-pH, or change the sign. Page 6773: The discussion on the relative sensitivity on pH to DeltaDIC is a bit of circular evidence since you have calculated DeltapH from DeltaDIC, but obviously with different TA etc. This is obviously the buffer capacity (betaDIC) that is different, as the authors explore later. Also, the difference in DeltaDIC and DeltapH is only meaningful if you add uncertainties to those numbers. With any realistic uncertainty to those numbers I doubt that you will find a significant difference.

References:

Álvarez, M., H. Sanleón-Bartolomé, T. Tanhua, L. Mintrop, A. Luchetta, C. Cantoni, K. Schroeder, and G. Civitarese (2014), The CO₂ system in the Mediterranean Sea: a basin wide perspective, *Ocean Sci.*, 10(1), 69-92. Takahashi, T., et al. (2009), Climatological mean and decadal change in surface ocean pCO₂, and net sea-air CO₂ flux over the global oceans (vol 56, pg 554, 2009), *Deep-Sea Res. I*, 56(11), 2075-2076. Yool, A., A. Oschlies, A. J. G. Nurser, and N. Gruber (2010), A model-based assessment of the TrOCA approach for estimating anthropogenic carbon in the ocean, *Biogeosciences*, 7(2), 723-751.

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