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Comment

***Interactive comment on* “The water column  
distribution of carbonate system variables at the  
ESTOC site from 1995 to 2004” by  
M. González-Dávila et al.**

**Anonymous Referee #1**

Received and published: 28 May 2010

Decision: This paper describes important time series observations. It can be published after major clarifications and revision.

General comments

This paper describes 10 years of time series carbon chemistry observations from the ESTOC site in the Sub-tropical N-Atlantic. Time series observations are very valuable at times of increasing atmospheric carbon dioxide when the oceanic response needs to be well documented and understood

The authors describe the carbon chemistry results both on the basis of their direct observations and they have also chosen to normalize total inorganic carbon, CT, and

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Alkalinity to salinity=35 (page 1999, line 3). There is no reason given for the normalization. It is evident from Fig. 8 that the observation data covers a salinity range from  $S < 35$  to  $S > 37$ , and that several water masses at various depths are involved. Here the normalization to  $S=35$ , the lower end of the observation range, means a substantial change in numeric values. Salinity normalization of carbon chemistry data ignores the effects of dissolution of biogenic carbonates, alkalinity inputs from rivers and may lead to relationships which do not reflect reality (Friis et al., 2003). Direct salinity normalization is really justifiable only when the salinity changes are solely due to evaporation or precipitation of water, i.e. cases where the AT-S relationship has a zero intercept. The authors must discuss the advantages and disadvantages of the salinity normalization if they conclude it is necessary for the interpretation of the observations. The interpretation basis needs to be sound, the present mixture of data and normalized data is confusing and unacceptable.

The narration on page 2003 of carbonate system variable distributions with depth and water masses is not vivid. Normalized pH<sub>25</sub>, NCT and NAT are used, and also unnormalized values, without any advantage being apparent with the normalizations. A graphic + verbal presentation is likely to be more informative.

The description, on pages 2005-2006, of variations in the rate of carbonate system changes with depth is based on 12 fixed depth levels. This is supplemented with Table 1 and figures 4, 5, which are crowded, and 6. The number of levels is superfluous, the uppermost 3, in the seasonally mixed layer, show essentially the same trends. It would be more interesting to present the surface layer and then base the description of the lower levels on hydrographic properties, water masses. Indeed, the authors venture into this path when they note NADW changes on page 206, line 23. Here again the advantage of normalization is not clear, if any. Table 1 includes both normalized and unnormalized data. The carbonate system species are calculated from normalized pH<sub>25</sub> and alkalinity as observed, page 2007, line 17.

Section 3.3 presents interesting results on anthropogenic carbon estimates. Firstly an

evaluation using the TrOCA method, presumably on unnormalized data. Secondly, on page 2013, a comparison of the TrOCA results with the rate of CT and NCT increase with time. The normalization question comes up here once more. The argument is based on that “oceanic and physical conditions are constant” (page 2013, line 4) and relatively constant potential density is invoked for the fixed depth levels. This appears to be unrealistic assumption, the reality is stated on page 2015, lines 9-12.

A new abstract will need to be written after the revision.

### Specific comments

P1996, line 22: The reference Bates, 2007 seems appropriate here.

P1999, line 7: The Experimental section should give a clear picture of the methods and procedures applied to ensure consistent quality information over the period of the time series. Thus information on precision evaluation and assessment of accuracy should be presented. The presentation here is unclear in many instances as listed in the following comments.

P1999, line 10: Fig. 1 would be more informative if the ESTOC location was shown on a chart of surface currents.

P1999, line 11: Description of the work conducted by German partners seems irrelevant if these observations are not used in this work.

P1999, line 20: Data and results are presented from depths >1000m, so “the first 1000 m” must be an inaccurate description.

P1999, line 24: Needs fuller information on CTD-SIS. Which CTD and what does SIS stand for?

P2000, line 1: How was the salinity determined in the water collected in Niskin bottles?

P2000, line 5: One would expect information on discrete fCO<sub>2</sub> sampling, or was fCO<sub>2</sub> only determined in the surface water flow system?

P2000, line 9: The standard deviation of 0.0015 is mentioned for determinations of CRM Batch #42 which was issued in 1995. Dickson Water is not certified for pH. Is this intended to be information on precision or accuracy?

P2000, line 13: CRM #32 was issued in 1995, #35 in 1996, #42 in 1997 and #46 in 1998. What QC procedures were applied for alkalinity 1998-2004?

P2000, line 14: “values that were within  $\pm 1.5 \mu\text{mol kg}^{-1}$ ”. Is this precision or accuracy?

P2000, line 18: What does the “residual of  $\pm 3 \mu\text{mol kg}^{-1}$ ” stand for. If it is the difference between calculated and CRM concentrations, then were corrections applied? How was the period 1998-2004 treated? Considering the precisions of the pH and Alk determinations what is the uncertainty associated with the CT calculation?

P2000, line 20: Were CRMs used with the CT determinations after 2004?

P2001, line 6: What is the “zero reading” gas?

P2001, line 12: Does the VOS-QUIMA line pass the ESTOC location?

P2001, line 16: Please clarify “standard error” for oxygen and “standard deviation” for nutrients.

P2005, line 1: The treatment on surface water fCO<sub>2</sub> is excessively long and the conclusion on rising surface fCO<sub>2</sub> trend is not convincing, in particular because the uncertainty for the 1995-2004 trend,  $1.55 \mu\text{atm yr}^{-1}$  (page 2004, line 6), is not given. What can be deduced about this trend from the air-sea fCO<sub>2</sub> difference?

P2006, line 5: Explain the calculation “fifth of the annual increase. . .”.

P2006, line 7: Why assume alkalinity when measurements exist?

P2007, line 9: It seems appropriate to compare this rate with other observations from the Sub-tropical N-Atlantic, e.g. (Bates, 2007).

P2007, line 12: The effect of temperature on the carbonate equilibria is well known but

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this comparison should provoke thoughts on the necessity of pH temperature normalization.

P2007, line 28: Calcium carbonate saturation is affected by pressure, fCO<sub>2</sub> and and temperature. Is the change in omega values only due to decrease in carbonate concentration?

P2008, line 7: If the authors can show that the “.. rate of change remains constant..” is a realistic model both on grounds of CO<sub>2</sub> emissions and sea water carbonate chemistry then the calculations that follow are presentable, otherwise not.

P2009, line 9: Section 3.2 is interesting. It appears from figures 9 and 10 that the profiles are created from mean results. The authors must reveal how the time series data are used in this section. Secondly, the questions on salinity normalization in General comments come up here again.

P2010, line 11: How does ATorg become NA Torg ?

P2010, line 25: How does RC . AOU become NC Torg ?

P2013, line 13: The argument for “increasing storage capacity” is not convincing. How do the authors define “storage capacity” and for what reason is it increasing?

P2016, line 2: Is the statement “general concordance . . . with others in the area“ a comparison with the BATS time series? If so, then reference is needed.

P2016, line 3: The final sentence states that the ESTOC site can be used by way of a reference to monitor anthropogenic carbon changes in the N-Atlantic Sub-tropical gyre. This statement cannot be presented without a substance. What are the criteria for reference stations which ESTOC supposedly fulfills? Have these criteria been put forward by international agencies?

Technical corrections

P1996, line 4: “anthropogenic properties” is a strange concept, seems better to use

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“anthropogenic signatures”.

P1996, line 10: “experimental values” better: “observed values”

P1998, line 13: “experimental” better: “observed”

P2001, line 20: Section 3.1 is far too long and could be broken up by subjects.

P2003, line 10: Is 2010 a typo, should it be 2100?

P2004, line 1: Suggest new subsection

P2005, line 6: Suggest new subsection

P2010, line 26: Typo: hard-issues

P2023: Fig. 2 The figures are small and of low resolution, the numbers are illegible even after zooming in.

#### References

Bates, N.R., 2007. Interannual variability of the oceanic CO<sub>2</sub> sink in the subtropical gyre of the North Atlantic Ocean over the last two decades. *J. Geophys. Res.*, 112, C09013(C09013).

Friis, K., Körtzinger, A. and Wallace, D.W.R., 2003. The salinity normalization of marine inorganic carbon chemistry data. *GEOPHYSICAL RESEARCH LETTERS* 1085, 33(2): doi:10.1029/2002GL015898.

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Interactive comment on Biogeosciences Discuss., 7, 1995, 2010.

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