Biogeosciences
Open Access
Discussions

Interactive comment on "Two decades of inorganic carbon dynamics along the Western Antarctic Peninsula" *by* C. Hauri et al.

C. Hauri et al.

claudinehauri@gmail.com

Received and published: 11 September 2015

MS No.: bg-2015-166: Two decades of inorganic carbon dynamics along the Western Antarctic Peninsula"

Line numbers refer to the track-change document (supplement)

This paper summarizes a large and long data set. The paper is descriptive and concludes that DIC drawdown is greatest inshore, redfield ratios are not always followed with nutrient depletion, and the balance of freshwater flux and biological production is a strong determinant of change in aragonite saturation state. The paper does not increase understanding of what was driving change in the region, but it is a useful descriptor of the variability in DIC and other carbon parameters. I did find at times the

relationship between the various parameters or why various some changes were selected to describe difficult to follow (see below). This caused me to have to stop reading and search through the paper for other information. For example, for most of the paper DIC, TA and nutrient data were available and why a TA vs salinity relationship was calculated in an early section was not apparent until later when salinity and year-round pCO2 measurements were used to calculate aragonite saturation state while the other measurements were Summertime only.

Response: We agree with the reviewer that the use of the salinity vs TA relationship was not clear. We therefore merged section 2.4 with section 3.4 and reworded the text. This should clarify that the TA-salinity relationship, in combination with surface pCO2 measurements, was used to calculate Ωarag for fall, winter and spring when DIC and TA bottle data are not available. Because nutrient data are also not available for these seasons, we did not use nutrients to predict salinity, even though we agree with the reviewer that it would probably improve the TA prediction. These changes were made to the following to paragraphs:

Lines: 536-557 "3.4 Seasonal variability To get insights into the carbon dynamics during winter, spring, and fall, when direct measurements of DIC, TA and nutrients are either scarce or not available, we developed a regional TA algorithm (based on PAL-LTER summertime data). In combination with seasonal LDEO pCO2, salinity and temperature data, we calculated Ωarag for the missing seasons. Due to the weak correlation between PAL-LTER temperature and TA ($r = 0.50$), we based the TA algorithm on salinity only (Figure A2, $r = 0.88$). Applying the Akaike information criterion [Burnham and Anderson, 2002], we determined that TA along the WAP will be best represented by a first order linear model. We then randomly divided the PAL-LTER surface measurements (depth <5 m) into 10 data subsets using the 10-fold cross validation method [Stone, 1974; Breiman, 1996]. Using 9 of the ten data sets we derived a regression model, predicted the TA with the model, and calculated the model coefficients and root mean square errors (RMSE). We repeated these steps so every data subset was left

out once. The coefficients for the final model were calculated from the mean of the ten regression coefficients. We found the best fit in the following equation: TApred (μmol kg-1) = 57.01 ($\pm$ 0.88) x S +373.86 ($\pm$ 35.26), which resulted in a linear correlation coefficient of r = 0.88 and a RMSE of 15.2 μmol kg 1 (Figure A2). In combination with the pCO2 measurement precision of 3 μatm, the RMSE of TA prediction resulted in a mean error in calculated Ωarag of 0.0219 units and pHT of 0.0043 [Glover et al., 2011]. Note that the calculated Ωarag and pHT estimates implicitly require that the approximately linear summertime TA-salinity relationship holds for the other seasons, a reasonable assumption if dilution and mixing substantially affect TA patterns."

The change in sea ice in the region is also mentioned a number of times in the paper, but there is no description of how sea ice is changing for the region (seasonally, interannual and spatial change over 20 years) apart from one sentence in the introduction. If there is more information on sea-ice change, it seems important to include and discuss the relevance in influencing the biogeochemical properties. Also, I was also not able to find a good description of the physical oceanography of the region data are presented from. Again, there are mentions here and there in the text, but it is scattered and difficult to follow.

Response: To address this comment we added text and several citations to the Introduction Section to better describe in more detail the regional ocean physical circulation.

Lines 98-110: "The physical oceanography of the region is strongly influenced by equatorward flow at the continental shelf/slope break associated with the eastward flowing Antarctic Circumpolar Current that abuts the continental slope along the WAP region. On the shelf, there are indications of one or more cyclonic circulation cells with poleward flow inshore [Hofmann et al., 1996; Dinniman and Klinck, 2004; Martinson et al., 2008]. Water mass properties are strongly influenced by subsurface intrusions onto the continental shelf of warm, nutrient and DIC rich Upper Circumpolar Deep Water (UCDW), that appears to be modulated by topographic depressions and canyons [Martinson et al. 2008; Dinniman et al., 2011; Martinson and McKee, 2012]. In win-

ter, respiration processes and the entrained deep CO2-rich water increase the DIC concentration in surface waters to supersaturated levels of CO2 with respect to the atmosphere [Carrillo et al., 2004; Wang et al., 2009; Tortell et al., 2014; Legge et al., 2015]."

Changes of sea ice and their potential influence on biogeochemistry are discussed in the introduction and discussion. Readers interested in more details on climate and sea-ice trends are referred to the cited articles including (Ducklow et al., 2007 and 2012; Stammerjohn et al., 2012).

Other comments: p 6931, lines 9-11: It is not clear how la Nina years influence the carbon cycle dynamics. Do more intense storms and a poleward displacement of the polar jet have an influence. There is a description of possible changes in carbon cycling for SAM. What does the literature indicate is happening to sea ice extent over the period?

Response: We adjusted the text in response to these questions> Lines 137-145: "During La Niña years, storms become longer and more intense, temperatures increase and sea ice extent decreases in the WAP region as a result of a strong low-pressure system driven by the poleward displacement of the polar jet [Yuan, 2004]. Positive SAM phases are also associated with positive temperature anomalies over the Antarctic Peninsula and decreased sea-ice extent [Kwok, 2002; Stammerjohn et al., 2008]. Furthermore, the SAM brings the Southern Hemisphere westerly winds closer to Antarctica, which amplifies the typical features of La Niña. During these periods, nutrient and CO2-rich Circumpolar Deep Water intrudes more frequently on to the shelf [Martinson et al., 2008], potentially increasing [CO2] on the shelf."

p 6933, section 2.1:Nutrient data are used in the paper, but I cannot find information on how these data were measured and where to access these.

Response: We agree with the referee that more detailed information about the nutrient sampling technique is required. To address this concern we added the following text:

Line 192-216 " "Water for inorganic nutrient analysis was subsampled from Niskin bottles into acid washed 50 mL Falcon tubes and frozen at -70 °C.. The samples were analyzed using a Lachat Quickchem 8000 autoanalyzer at the University of California at Santa Barbara Marine Science Institute Analytical Lab from 1993 2007 and later at the Marine Biological Laboratory (Woods Hole MA, 2008 – 2012). Inorganic nutrient data reach a precision of ± 1%. All PAL-LTER data and a detailed description of the sampling methodology are publicly available at http://pal.lternet.edu/ (dissolved inorganic nutrients, PAL LTER dataset 27)."

p 6935, line 7: how many outlier (per cent) were excluded out of the total number of samples? The text suggests there may be an analytical problem. I suspect this isn't the case, but the sentence beginning "These outliers included..." indicates there were many more than described in the section.

Response: There were only 4 outliers. We agree that this sentence was confusing and adjusted it (Lines 263-265): "Four PAL-LTER pCO2 outliers that underestimate/overestimate pCO2 relative to the underway observations by more than 150 μatm were removed."

p 6935, lines 10-19: I am not sure what the point of this regression analysis broken down into different years is. I first thought the intercept might be meaningful, but it seems more like the authors are trying to check the internal consistency of their measurements. Why not consider the residuals? Is the need to split the years used to compare pCO2 measured and pCO2 calculated an indication that the quality of the measurements has issues some years? If so, please state what years and why?

Response: In this paragraph we are discussing potential reasons why the correlation between the calculated PAL-LTER pCO2 and the measured LDEO pCO2 is not >0.82. Among matching issues and the resulting large pCO2 set-offs, we believe that years with a smaller range of pCO2 variability may be responsible for a large error of the intercept parameter, leading to a lower correlation. We agree that this may be confusing

C5242

and not useful and therefore adjusted text and figure accordingly.

Lines 265-273: "Analysis of the corrected data set with a Linear Regression Type II model suggests a correlation of r = 0.82 (Figure A1, Table 1). Some of the observed discrepancies may be attributed to errors in matching the times of bottle samples with those of underway pCO2 measurements. Seawater inorganic carbon chemistry is highly variable along the WAP due to the influence of productivity, respiration, freshwater and upwelling of CO2-rich subsurface water [Carrillo et al., 2004]. Small matching errors may therefore introduce small DIC and TA offsets, which would translate into larger fractional differences in pCO2 due to the large Revelle Factor (∂ ln pCO2/ ∂ ln DIC) common in the region [Sarmiento and Gruber, 2006]"

P 6936, section 2.4: Why are nutrient concentrations ignored in the TA vs salinity relationship given what appears to be a large range in pCO2 and presumably nutrient concentrations? Nutrient data are used with TA on page 6939. I am also unclear on the relevance of this salinity vs TA relationship. Most of the following sections in the paper do not seem to use the relationship as there are TA, DIC and nutrient data used to calculate the carbonate system parameters, or is this incorrect? Section 3.4 does use the relationship and it would be helpful to state in section 2.4 that it is used later with data pCO2 data to calculate the saturation state in fall, winter and spring seasons when bottle data are not available.

Response: We agree with the reviewer that the use of the salinity vs TA relationship was not clear. We therefore merged section 2.4 with section 3.4 and reworded the text. This should clarify that the TA-salinity relationship, in combination with surface pCO2 measurements, was used to calculate Ωarag for fall, winter and spring when DIC and TA bottle data are not available. Because nutrient data are also not available for these seasons, we did not use nutrients to predict salinity, even though we agree with the reviewer that it would probably improve the TA prediction. These are the first two paragraphs of the newly merged section 3.4:

C5243

Lines: 536-557 "3.4 Seasonal variability To get insights into the carbon dynamics during winter, spring, and fall, when direct measurements of DIC, TA and nutrients are either scarce or not available, we developed a regional TA algorithm (based on PAL-LTER summertime data). In combination with seasonal LDEO pCO2, salinity and temperature data, we calculated Ωarag for the missing seasons. Due to the weak correlation between PAL-LTER temperature and TA (r = 0.50), we based the TA algorithm on salinity only (Figure A2, r = 0.88). Applying the Akaike information criterion [Burnham and Anderson, 2002], we determined that TA along the WAP will be best represented by a first order linear model. We then randomly divided the PAL-LTER surface measurements (depth <5 m) into 10 data subsets using the 10-fold cross validation method [Stone, 1974; Breiman, 1996]. Using 9 of the ten data sets we derived a regression model, predicted the TA with the model, and calculated the model coefficients and root mean square errors (RMSE). We repeated these steps so every data subset was left out once. The coefficients for the final model were calculated from the mean of the ten regression coefficients. We found the best fit in the following equation: TApred (μmol kg-1) = 57.01 ($\pm$ 0.88) x S +373.86 ($\pm$ 35.26), which resulted in a linear correlation coefficient of r = 0.88 and a RMSE of 15.2 μmol kg 1 (Figure A2). In combination with the pCO2 measurement precision of 3 μatm, the RMSE of TA prediction resulted in a mean error in calculated Ωarag of 0.0219 units and pHT of 0.0043 [Glover et al., 2011]. Note that the calculated Ωarag and pHT estimates implicitly require that the approximately linear summertime TA-salinity relationship holds for the other seasons, a reasonable assumption if dilution and mixing substantially affect TA patterns."

p 6937, section 3.1: This is OK, but it averages data from the Summer, when there is large variability. The point that there are large and persistent decreases inshore relative to offshore is well defined. However, the section does not indicate the range of values used in the averaging. For example, what range of sDIC and salinity values occurs inshore compared to offshore for the averaged data points. It would be good to get some idea of the variability.

Response: We agree with the reviewer that this section should describe the large inter annual variability. We adjusted the text accordingly: Lines 362 -371: "Surface waters in the PAL-LTER region exhibited high spatial and interannual variability of DIC (min = 1850 μmol kg-1 and max = 2173 μmol kg-1), TA (min = 2087 μmol kg-1 and max = 2396 μmol kg-1), and salinity (min = 30.3 and max = 33.9) across the shelf. As a result, surface Ωarag reached levels as low as 0.98 in 1996, while maximum Ωarag values were > 3 in several years (Figure 3). Off-shore, DIC (min = 2072 μmol kg-1 and max = 2255 μmol kg-1), TA (2265 μmol kg-1 and 2355 μmol kg-1), and salinity (min = 33.4 and max = 34) were less variable, resulting in a smaller Ωarag range (min = 1.14 and max = 2.41). Additional aragonite undersaturation was detected between 100 and 200 m depth in 2005 and 2007 (Figure 3). At depths > 70 m, which is below the mixed layer depth, Ωarag was < 1.5 in all years."

p 6939, line 16: A reference to Wolf-Gladrow et al (2007) Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, Marine Chemistry, 106 (1-2), 287-300 is appropriate here.

Response: We agree and added the citation: Lines: 470-472: "According to the Redfield ratios (C/N/P = 106:16:1, [Redfield, 1958]), photosynthetic utilization of 1 mole of NO3 increases TA by 1 umol kg-1 [Wolf-Gladrow et al., 2007] and decreases DIC by 106/16 (6.6)."

p 6943, line 6: I could not find any mention in the Anderson et al 2000 paper on how glacial meltwater influences aragonite saturation state. It is in the Yamamote-Kawai paper.

Response: We think that the Anderson paper is an appropriate citation here as it presents a nice dataset of alkalinity measurements from glacial streams. Both citations refer to the fact that DIC and TA are much lower in sea ice (Yamato-Kawai) and glacial Anderson) meltwater. The part of the sentence that mixing of seawater with meltwater leads to dilution of [CO32-] is an explanation for the reader of the effect of

lower TA and does not need a citation.

p 6944, lines 11-12: These refer to DIC drawdown in the WW layer as biological, which seems reasonable as an ultimate cause of drawdown. I suppose this drawdown will occur in the summer season? Is this correct and why can't the DIC decrease in Figure 5 be due to mixing of surface water into the WW layer or mixing of lower DIC WW water from other regions.

Response: We agree with the reviewer that in addition to biological DIC drawdown in the WW layer, other physical mechanisms may have an influence. For example, vertical mixing could play a role either by mixing in low DIC surface waters during the summer or during the prior winters when low DIC surface water is contributing to the formation of winter water, which then carries a signal of past surface productivity.

Lines 758-762: "The observed DIC drawdown in the winter water (Figure 5 and A3) may be a result of biological productivity, which is supported by previous observations of Chl a maxima in the euphotic part of the winter water, likely due to increased iron concentrations there [Garibotti et al., 2003; Garibotti, 2005]. However, it is also likely that lateral advection or vertical mixing of low DIC water into the winter water have caused this signal.

p 6944, lines 14-18: Is the text here referring to Figure 5? This is the only figure I could locate that shows anything that might relate to the text.

Response: This text does not refer to a specific figure. The information was taken out of a numerical analysis and discusses the low levels measured off-shore (see section 3.1). We now mention that there is no figure for this statement. Lines 764-766: "Low Ωarag values (< 1.35) observed offshore coincided with surface waters supersaturated with regard to atmospheric CO2, salinities >33.5, and temperatures between 1.3 – 1.5 °C (not shown)."

p 6945, lines 10-25: Why would not accounting for the drivers of TA influence the TA vs

C5246

salinity relationship? If TA+nutrients are used, it may help the relationship with salinity, but the authers have not done this. Invoking ikaite is unlikely to explain the differences. The occurence of ikaite in sea ice is limited and it is not clear how changes in a 1-2 m sea ice layer spread over a 50m mixed layer could have much effect (ie any effect would be diluted in the 50m thick mixed layer). This section is not much more than a statement that TA variability could be explained by just about any process. One other possible explanation is the TA measurements have a large amount of error although the methods section states the measurements are high accuracy.

Response: We constructed the TA relationship to estimate seasonal TA and Ωarag. Because there are no nutrients available for the other seasons, there was no use in constructing a TA relationship based on nutrients. This is now more clearly described in the following lines:

Lines 536-540: "To get insights into the carbon dynamics during winter, spring, and fall, when direct measurements of DIC, TA and nutrients are either scarce or not available, we developed a regional TA algorithm (based on PAL-LTER summertime data), and in combination with seasonal LDEO pCO2, salinity and temperature data, calculated Ωarag for the missing seasons"

We don't see why we can't discuss potential reasons for the large TA variability and therefore did not change the text.

p 6946 line 16-20: Why have two high values been singled out to consider the decadal rates of change in the central sub-region? The fall and spring are when rapid change might occur and it is not clear from Table 3 or the text if this is a persistent pattern each year or due to limited data. The more interesting data may be for winter when biological effects are small compared to Spring. Here, the decadal trend is small in the central region and similar to the atmospheric increase in the north region. Do these changes agree with Takahashi's previous estimates and why the differences? The same applies to the fall and spring rates of change (ie why the regional differences?).

C5247

Response: We redid the trend analysis based on the corrected version of the LDEO pCO2 data set that was recently published (Takahashi et al., 2015). Furthermore, we restricted our analysis to the central sub-region, which corresponds with the LTER sampling region. As a result, none of the trends are significant anymore, which shows how difficult it is to distinguish between real secular trends and natural variability. It also corresponds with analysis done by Munroe et al., [in press]. This correction led to a variety of adjustments in the text and table 3:

Lines 55-58: "Even though we did not detect any statistically significant long-term trends, the combination of ongoing ocean acidification and freshwater input may soon induce more unfavorable conditions than the ecosystem experiences today."

Lines 630-637: "3.5 Temporal trends Trend analysis of the PAL-LTER data showed no statistically significant annual trends (at the 95% confidence level) in the measured carbon parameters, temperature or salinity in surface waters in summer between 1993 and 2012 (Table 2). As a comparison, we conducted a trend analysis for the LDEO surface underway pCO2 data set (1999 – 2013) in the same region. LDEO observations show an increasing, but not statistically significant trend in surface pCO2, supporting our results above (Table 3). The largest increasing trend was found in fall, (1.9 ± 0.95 μatm yr-1), but this trend was also slightly outside the confidence interval and therefore statistically not significant."

Lines 790-804: "The large uncertainties in our estimated temporal trends are caused inherently by the large spatial and temporal variability of our data. Nevertheless, our mean rates of 1.45 ± 2.97 for summer and 0.43± 0.77 μatm yr-1 for winter suggest that the surface water pCO2 has been increasing at a slower rate than the atmospheric pCO2 rate of about 1.9 μatm yr-1, and that the air-to-sea CO2 driving potential has been increasing. Our results may be compared with the recent analysis of the 2002-2015 time-series data obtained across the Drake Passage by Munro et al. [in press]. In the waters south of the Polar Front (their Zone 4, closest to the LTER area), they observed that the surface water pCO2 increased at a rate of 1.30 ± 0.85 μatm

yr-1 in summer and 0.67 ± 0.39 μatm yr-1 in winter, which are comparable with ours along the WAP. We observed the strongest but still insignificant increase in surface pCO2 in fall (1.9 μatm year-1, p = 0.0685). This increase corresponds with the mean atmospheric pCO2 increase of 1.9 μatm per year, which causes a pHT decrease of about 0.02 per decade [Takahashi et al., 2014]. Interestingly, Stammerjohn et al., [2008a, 2008b] found that sea ice extent and wind are also changing most rapidly in spring and fall, which may enhance sea-air gas exchange and therefore facilitate positive pCO2 trends. Furthermore, it is likely that the strong counter effect of biological productivity successfully masks the pCO2 trend in summer, and decreased gas exchange due to sea ice weakens the trend in winter. However, the WAP climate and oceanography are regulated by large-scale atmospheric patterns, such as El Niño Southern Oscillation and Southern Annular Model [Stammerjohn et al., 2008a], which may also influence the region's inorganic carbon chemistry on an interannual scale. A longer measurement period may be needed in order to be able to distinguish with certainty between natural variability and secular trends [Henson et al., 2010]."

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/12/C5238/2015/bgd-12-C5238-2015-supplement.pdf

---

Interactive comment on Biogeosciences Discuss., 12, 6929, 2015.