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Biogeosciences Discussions

Interactive comment on "High temporal and spatial variability of dissolved oxygen and pH in a nearshore California kelp forest" *by* C. A. Frieder et al.

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Response to the review by Anonymous Referee #2

We would like to thank the anonymous referee for a thorough review and general suggestions that will improve the quality of this manuscript. In the following sections, comments originating from the reviewer will be given in italics, and text in quotations is intended to be included in manuscript revisions.

Specific Comment 1

In order to constrain the ocean carbonate system, 2 of the 4 possible parameters must

be directly measure... or estimated using robust empirical relationships with other measured parameters. Recently, the international ocean acidification observation community defined constraint of the carbonate system as a minimum requirement of an observational site for understanding ocean acidification conditions... This issue could be addressed by one of the following:

a. Include a more detailed discussion about the limitations of using only pH measurements to assessing ocean acidification conditions and attributing impacts.

b. Estimate temporal and spatial variability of pCO2 and Ω using discrete TA and DIC validation data... The authors may also want to explore whether it is possible to use the algorithms developed by Alin et al. JGR 2012 for the southern CCS to estimate carbonate system parameters. This may not be ideal for nearshore waters, but it's possible the algorithm could work in deep water using pH, DO, and SSTC measurements made in the kelp forest. This could be tested by comparison to discrete samples made during the study.

We have explored whether it is possible to use the algorithms developed by Alin et al. (2012) for 15 to 500 m water depth for the southern California Current to estimate carbonate system parameters for the inshore kelp forest and adjacent shelf at depths of 7 to 17 m. We compared TA determined from calibration samples taken next to the SeapHOx sensor with calculated TA based on the algorithms provided in Alin et al. (2012). Measured TA is consistently greater than calculated TA (Figure 1), and so these algorithms are apparently not sufficient to calculate TA from salinity and temperature in this nearshore setting.

Instead, we calculate pCO_2 and Ω from measured pH, salinity and temperature data along with an upper and lower estimate of total alkalinity (TA) for the La Jolla Kelp Forest (LJKF). The lower and upper values chosen for TA were 2225 and 2260 μmol kg^{-1}. These values are 5 μmol kg^{-1} beyond that observed from the minimum and maximum values from all discrete samples taken for SeapHOx calibration purposes (n

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= 18). Additionally, these values fall within the range reported by Alin et al. (2012) for TA < 100 m water depth. We feel that this is a conservative approach to calculating carbonate chemistry parameters because we are incorporating the full range of TA observed during the time period of the study, which provides a range of possible pCO_2 and Ω values.

For Methods: "pCO_2, Ω_{arag}, and Ω_{calc} were estimated from the high-frequency pH, temperature, and salinity data generated by the SeapHOx at 7 m and 17 m water depth at mooring A along with an upper and lower estimate of TA for the LJKF. The lower and upper values chosen for TA were 2225 and 2260 μmol kg^{-1}. These values are 5 μmol kg^{-1} beyond that observed from the minimum and maximum values from all discrete samples (n = 18) taken for SeapHOx calibration purposes. Additionally, these values fall within the range reported by Alin et al. (2012) for TA < 100 m water depth. Carbonate chemistry parameters were calculated using the Matlab version of CO2SYS (van Heuven et al. 2011). Using the upper and lower limit of TA for this system along with pH, temperature and salinity data resulted in an average range for each calculated value of pCO_2 of 8 μatm. The average ranges for each calculated value of Ω were 0.031 for Ω_{arag} and 0.049 for Ω_{calc}."

For Results: "pCO_2, Ω_{arag}, and Ω_{calc} were estimated using sensor data collected at 7 m and 17 m during the depth experiment (data used corresponds with Fig. 5) along with TA ranges specific to this system. At 7 m water depth, estimated pCO_2 ranged between 246 and 820 μatm, and between 353 and 1016 μatm at 17 m water depth (Fig. 2). At 7 m water depth, estimated Ω_{arag} ranged between 1.15 and 3.05, and ranged between 0.90 and 2.45 at 17 m water depth (Fig. 2). At 7 m water depth, estimated Ω_{calc} ranged between 1.81 and 4.78, and ranged between 1.41 and 3.83 at 17 m water depth (Fig. 2). The highest pCO_2 and lowest Ω corresponded with the lowest DO and pH conditions observed."

For Discussion: "Increasing evidence suggests that species responses to ocean acidification vary for different carbonate system constituents (Fabry et al. 2008, Doney et al.

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2009). Thus full constraint of the carbonate system, beyond just pH measurements, is critical for defining this nearshore system and the potential sensitivity or resilience of its residents to ocean acidification. The observed range in TA in the LJKF (35 μmol kg^{-1}) has relatively little influence on variability in pCO_2 in this system; instead changes in pCO_2 are driven by large DIC gradients. Ω_{arag} was undersaturated at 17 m for a short period of time at the end of February and early March, 2011. This also corresponded with the lowest DO concentrations observed (Fig. 5). While emphasis has been placed on the strong relationship between DO and pH, low DO also corresponds with low Ω_{arag}, low Ω_{calc}, and high pCO_2."

Specific Comment 2

The authors make the conclusion that "these findings raise the possibility that the benthic communities along eastern boundary current systems are currently acclimatized and adapted to natural, variable, and low DO and pH" (lines 26-28 of abstract). While this may be true, this paper should include additional discussion on variability, with references to studies that have observed variable pH at other coastal sites...

We have included reference to recent studies that have observed variable pH at other coastal sites within the Introduction and reference these papers in the Discussion section. Below is a summary of general findings, with emphasis on kelp forests, to be included in the Introduction at the end of the third paragraph:

"Some high-frequency variability in pH has been reported in nearshore habitats (Hofmann et al. 2011b, Yu et al. 2011, Booth et al. 2012). Results indicate that pH signatures are ecosystem and site-specific with characteristic diel, semidiurnal, and stochastic patterns of varying amplitudes. Kelp forests in upwelling regions can exhibit large fluctuations in pH conditions due to a combination of mixing, tidal excursions, upwelling, and biological activity (Hofmann et al. 2011b)."

...and how variability may change if anthropogenic CO2 continues to increase into the future... The statement of acclimatization of benthic communities should also be

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considered in the context of predictions of bottom water undersaturation in the CCS by Gruber et al. Science 2012.

At this point in time there is uncertainty as to how variability patterns will change if anthropogenic CO_2 continues to increase into the future, and changes in variability will likely be influenced by changes in water-column stability, the P:R ratio, upwelling dynamics, wind patterns, etc. The fourth, fifth and sixth paragraph of the Biological Implications section in the Discussion now reads:

"It is unclear which aspect of the DO and carbonate chemistry signals will shape ecological patterns and how these aspects are changing over time. Changes in the extremes, ranges, or patterns of variability need to be considered in the context of organismal sensitivity. Knowledge of DO thresholds and responses to low DO events by shelf animals in this region is limited and in need of further study, while our present understanding of organism and ecosystem sensitivity to carbonate chemistry is in relation to mean conditions. Laboratory studies. . ."

"Our P:R model predicts that under future scenarios of ocean acidification pH could be as low as 7.35 (corresponding pCO_2 approximately 2100 μatm) at low DO concentrations. This drop could mean that carbonate chemistry will play a larger role in structuring marine ecosystems than DO if DO conditions remain the same over this time period. Yet while pH may reach extreme low levels, the variability associated with these mean changes is unknown. When just considering changes in the pH and oxygen relationship due to ocean acidification, high-frequency in pH variability would increase relative to present-day variability. This is because in this system, changes in pH are largely driven by changes in DIC. The same change in DIC at high concentrations will produce a greater change in pH than at low concentrations of DIC." *See Author Comment reply to Melzner for description of P:R model.

"Still, there are many other processes that may change over the coming decades that will structure pH and oxygen dynamics. These include changes in water-column stabil-

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ity, the P:R ratio, upwelling dynamics (e.g. timing and intensity), wind patterns, and the sources and chemical properties of water that is advected horizontally and vertically into upwelling margins. Model simulations of the California Current System indicate that the seafloor (50 - 120 m) will become exposed to year-round aragonite undersaturation by 2050 (Gruber et al. 2012). Additionally, future changes in upwelling dynamics in the SCB remain a critical topic for further research. Evidence suggests a general intensification of wind-driven coastal upwelling in major upwelling regions as greenhouse gas concentrations increase (Bakun et al. 2010, Narayan et al. 2010). These results suggest that DO could reach hypoxic values at increasingly shallower depths and result in habitat compression (or expansion) for intolerant (or tolerant) species. We suggest that in eastern boundary current systems that biological sensitivity to changes in DO and pH will largely derive from changes that carry low DO and pH waters from depth into nearshore benthic habitats (Feely et al. 2008, Gruber 2011, Hofmann et al. 2011a)."

. . .without that discussion, these statements comparing nearshore and open ocean systems are out of context and confusing and should be removed (or modified).

We have removed line 12-13 in Abstract because comparison of open ocean and nearshore systems is out of context without discussion of variability. We now discuss uncertainty as to whether marine organisms will respond to some threshold in pH, a decreasing mean over a long time period, lower minimum values, larger fluctuations, etc. (see above).

Specific Comment 3

The paper would be much improved with additional discussions of research findings on high-CO2 impacts on kelp and potential changes to future upwelling. Reference is made to macrophyte-based ecosystems being refugia to deoxygenation and acidification; however, there should be some discussion in the Introduction of section 4.4 on the potential impacts of changing chemistry on kelp (or macrophytes in general; e.g.

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increased photosynthesis due to increasing pCO2)... Reference is also made to future intensifying of upwelling, but there is no explanation of this potential phenomenon. . .

We have incorporated potential impacts of high CO_2 on kelp in the Introduction by discussing the findings of relevant studies and recent reviews (e.g. Harley et al. In Press). We agree that it is important to highlight the changes that macrophyte-dominant systems may undergo in future high-CO_2 scenarios. We have included the following text at the end of the 4th paragraph in the Introduction:

"Additionally, it is important to identify present-day carbonate chemistry conditions in coastal macrophyte-dominated ecosystems as recent evidence suggests that under high-CO_2 scenarios kelps have variable but often positive responses to elevated CO_2 (Swanson and Fox 2007, Roleda et al. 2012). A working hypothesis for kelps in the SCB is that they may respond positively to the direct and indirect effects of ocean acidification but negatively to the direct and indirect effects of warming (Harley et al. In Press). Still, other evidence suggests that under high-CO_2 scenarios canopy-forming macroalgae could experience greater competition with noncalcareous turf species (Connell and Russell 2010, Hepburn et al. 2011)."

We have also incorporated references that provide evidence of intensified upwelling along eastern boundary upwelling systems in response to greenhouse gases. See text above in Specific Comment 2 that includes incorporation of these references.

Technical Corrections

1) Lines 8-9 Introduction: Ocean acidification is not only decreasing pH but decreasing saturation states as well.

We have added Ω to this sentence. This is particularly relevant for us to include since we are now presenting time-series data for calculated Ω_{arag} and Ω_{calc} in the manuscript.

2) Line 21 section 2.2: Were discrete samples taken at deployment and recovery to define sensor drift, if any?

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The calibration samples were collected via SCUBA next to the sensor with a 5L niskin bottle during the middle and/or end of the sensor deployment, and not at the beginning because we found the pH sensor requires a day before providing reliable data. When two calibration samples were taken during the same SeapHOx deployment, they were averaged since we didn't find significant evidence of drift and these sensors have been shown to be stable for months at a time (Martz et al. 2010). This information is now included in section 2.2.

3) Line 28 section 2.2: Define constants used in CO2 SYS here.

pH was calculated from TA and DIC using the Matlab version of CO2SYS (van Heuven et al. 2011) with dissociation constants from Mehrbach et al. (1973) as refitted by Dickson and Millero (1987).

4) Line 21 section 4.2: Del Mar buoy should be defined earlier – it appears as "DM buoy" in previous sections.

Thanks. We now define Del Mar buoy the first time it is presented.

5) Line 9 section 4.3: P:R is defined here, but should be defined in earlier sections.

P:R is now defined the first time it is presented in the manuscript.

6) Line 26-27 section 4.4: I believe there is experimental evidence that some organisms actively buffer sites of calcification, such as in shellfish and corals (Cohen and Holcomb Oceanogr. 2009).

We were intending for this paragraph to focus solely on studies that investigate early-life stages of species that are resident to the San Diego region. This is why this paragraph is focused on the findings of Gaylord et al. (2011) and O'Donnell et al. (2010). We have now clarified this in the text of the manuscript and also included results from Sunday et al. (2011).

7) Lines 16-17 section 4.4: Gruber et al. Science 2012 have demonstrated this in CCS

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models. Should be referenced to here.

Thanks. These findings from the CCS models from Gruber et al. (2012) have been included into this section with particular emphasis on saturation state at the seafloor. See Specific Comment 2 above for text.

8) Figure 9. This figure is a bit confusing. Why isn't the $\triangle$pH and $\triangle$DO ranges as large as the ranges observed during this study?

To strengthen the overall paper and minimize possible confusion for readers we have decided to remove this figure. The ranges reflected in the figure represented mean changes, and this is why the extreme ranges were not included.

Figure Captions

Figure 1. Measured total alkalinity (TA) from discrete samples taken next to SeapHOx sensors for calibration purposes and TA calculated from salinity and temperature (T and S data from sensor corresponding to the time when discrete sample was taken) using algorithms provided by Alin et al. (2012) to estimate carbonate system parameters in the southern California Current System. The solid black line is the 1:1 relationship between TA measured and TA calculated. (Figure not included in revised manuscript)

Figure 2 (Figure 10 in revised manuscript). Estimates of pCO_2 and saturation state of aragonite and calcite (Ω_{arag} and Ω_{calc}) at 7 m (grey) and 17 m (purple) water depth at mooring A during two separate deployments. The width of the line at each point represents the range estimated for pCO_2 or Ω as calculated from pH, temperature, and salinity measured by the SeapHOx sensor and a TA range of 2225 – 2260 μmol kg^{-1}.

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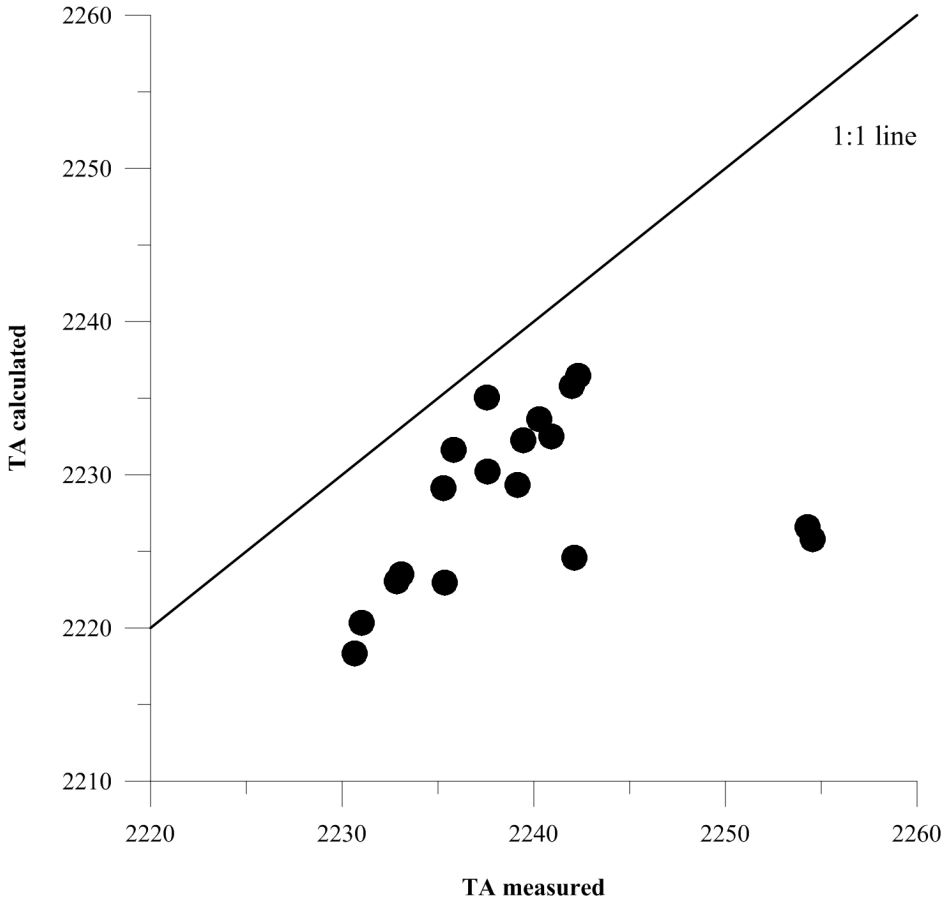

Fig. 1. See figure caption above.

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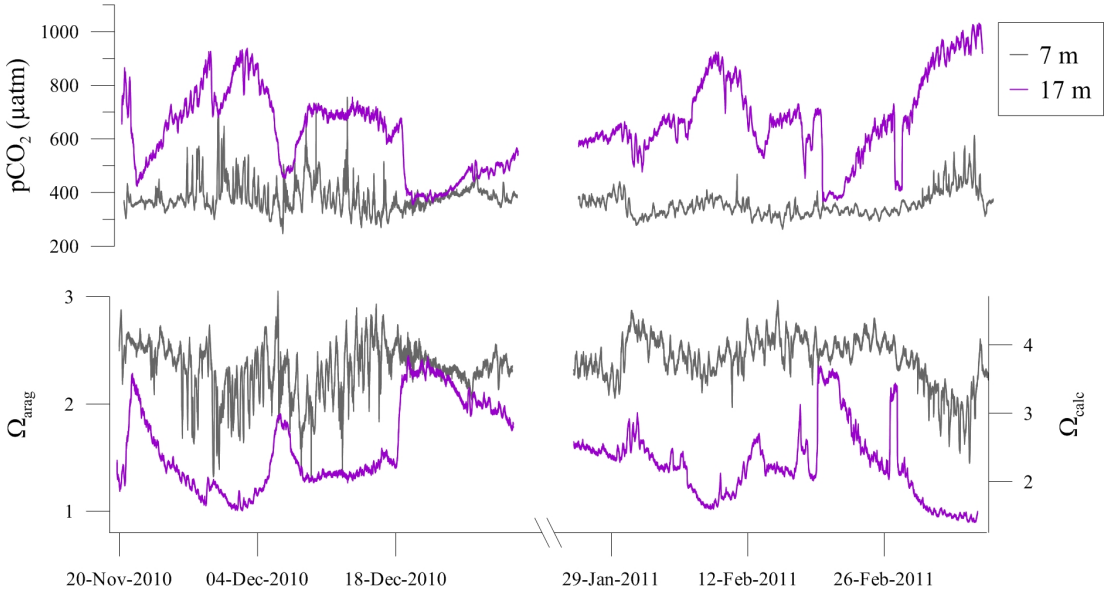

Fig. 2. See figure caption above.

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