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 Frank Melzner

We would like to thank Frank Melzner for his generous time in reviewing our manuscript and useful suggestions to improve its quality and relevance. 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.

General comment 1

The authors should keep in mind that for most marine metazoans, CO2 and O2 partial pressures are the most important parameters that impact biological processes... a change in pH by 0.2 units can have very different impacts on marine animals depending on whether one considers a change from e.g. 8.3 to 8.1 or one from 7.7 to 7.5, as the change in pCO2 is very different between these two intervals. Hence, I would recommend to add a figure / table on estimated changes in pCO2 calculated from measured alkalinity / dissolved inorganic carbon and / or pH.

Given the importance of changes in pCO2 and saturation state (Ω) on biological processes, we have estimated both pCO2 and Ω for calcite and aragonite. This was done by calculating pCO2 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 = 18). Additionally, these values fall within the range reported by Alin et al. (2012) for TA < 100 m water depth. The below figure is incorporated into the revised manuscript (Figure 1). There is also a description of the calculations made in the Methods section, and the results are summarized in the Results section. We feel that this is a conservative approach to calculating other carbonate chemistry parameters because we are incorporating the full range of TA observed during the time period of the study, which provides a range for each pCO2 and Ω value calculated.

For Methods: \( \text{p}^{\text{CO2}}, \Omega_{\text{arag}}, \text{and } \Omega_{\text{calc}} \) 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.
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. 1). 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. 1). 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. 1). 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. 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$_2$.”

General Comment 2

... The authors might include some calculations on the magnitude of change in pCO2 / pH to be expected in the future based on estimated increases in future dissolved inorganic carbon...

We have estimated the magnitude of change in pH expected for the year 2100 (800 ppm) and the result this will have on the production and respiration relationship between DO and pH following the methods of Cai et al. (2011). A photosynthesis and respiration model had already been included in Fig. 6 to explain the relationship between DO and pH. Adding on that, we have modeled the projected changes in pH under future conditions:

“The P:R model was then run under future atmospheric CO$_2$ conditions at 800 ppm (year 2100) using the same alkalinity, salinity, and temperature conditions but with an increase in DIC (+ 112 µmol kg$^{-1}$) at oxygen saturation. This model attributes all of the change in pH to anthropogenic CO$_2$ intrusion. At DO saturation, pH is expected to decrease by 0.20 units, while at low DO values, pH could be as low as 7.35, a decrease of 0.37 pH units from present low pH conditions. The additional drop in pH at low DO is a consequence of the nonlinear nature of the carbonate system (Cai et al. 2011, Melzner et al. 2012). Nearshore CO$_2$-enriched habitats are expected to experience greater changes in pCO$_2$ than the open surface ocean and have been suggested to be particularly vulnerable habitats in a changing ocean climate (Brewer and Peltzer 2009, Thomsen et al. 2010, Cai et al. 2011).”

Figure 2 includes the modelled decreases in pH with OA, and is now one of the main figures of the manuscript. Given this added importance, we have pulled it from its current location (Fig. 6 panel c) and made it a solo figure. We then adjust Figure 6 to include panel a, b, e, and f, because these results are important findings, and remove panel d to avoid extraneous figures that we feel do not strengthen the overall paper.

Minor Comments

P4115, line 26: for many species that are poor at controlling extracellular pH it is clear that rapid changes in seawater pCO2 rapidly translate into changes in extracellular pCO2 and pH...
We have expanded the discussion section – Biological implications of dissolved oxygen and pH trends – to consider how different types of marine metazoans have differential capability to actively regulate extra- and intracellular pH in response to rapid changes in seawater pCO₂ / pH.

"pH and DO in the LJKF vary on multiple timescales with large ranges; biological responses to pH and DO also unfold over a range of timescales. Rapid pH and DO changes can disturb an organism's extracellular and intracellular acid-base balance, and in the LJKF these changes can be as great as 62 µmol O² kg⁻¹ h⁻¹ and 0.16 pH units h⁻¹. Different taxa react differently to these rapid excursions. For example, mussels cannot control extracellular pH (Thomsen et al. 2010), sea urchins take several days to adjust (Stumpp et al. 2012), and many fish and decapod crustaceans are able to rapidly regulate extracellular and intracellular pH (Heisler 1984). The low values of DO and pH observed at 17 m for week-long durations in the LJKF are likely not biologically significant under present conditions. However these low values of DO (< 90 µmol kg⁻¹) are considered to be sublethal thresholds for coastal species of fishes, crustaceans, and bivalves (Vaquer-Sunyer and Duarte 2008). These groups are common and diverse within the kelp forest at depths deeper than 17 m where even lower DO concentrations occur (Parnell et al. 2006)."

"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…"

*Figure 9 should be expanded to reflect full range of pH / pCO2 changes observed in this study and should reference published example of process sensitivity to the pH / pCO2 / pO2 changes depicted in the figure*

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.

Papers that could be discussed:

We have included the following papers into the manuscript based on reviewer's suggestions:

*Cai et al. 2011 Nature Geoscience*

This paper has been incorporated into the second paragraph of the introduction as an example of the tight relationship between oxygen and pH. We have also included discussion of Cai et al. 2011 into changes in the oxygen and pH relationship as a function of ocean acidification (see General Comment 2 above).

*Brewer and Peltzer 2009 Science; Thomsen et al. 2010 Biogeosciences*

See reply to General Comment 2 that includes addition of above references.

*Feely et al. 2010 Estuarine Coastal Shelf Science; Haynert et al. 2011 Mar Ecol Prg Ser*

The above studies were suggested as examples of carbonate chemistry dynamics in nearshore regions. We have included other studies that incorporated similar approaches to observing oxygen and carbonate chemistry dynamics, and felt that these studies were more relevant to the methods of this paper than the above (Hofmann et al. 2011, Cullison Gray et al. 2011, Yu et al. 2011, Booth et al. 2012).

*Bechmann et al. 2011 J. Toxicol. Env. Heal. A; Gazeau et al. 2010 Biogeosciences*

There are a range of published ocean acidification studies that focus on a variety of taxa. We wanted to include those that focused on species that are resident to coastal San Diego and thus did not include the above suggested studies.
“Another study on a resident urchin, *Strongylocentrotus franciscanus*, investigated the potential for evolutionary response in larval development to ocean acidification and found that *S. franciscanus* larvae were smaller but that phenotypic and genetic variation could allow evolutionary responses within 50 years in response to a pH decrease of 0.31-0.33 units (Sunday et al. 2011).”

**Figure Captions**

Figure 1 (Figure 10 in revised manuscript). Estimates of pCO$_2$ and saturation state of aragonite and calcite ($\Omega_{\text{arag}}$ and $\Omega_{\text{calc}}$) 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 $\Omega$ as calculated from pH, temperature, and salinity measured by the SeapHox sensor and a TA range of 2225 – 2260 $\mu$mol kg$^{-1}$.

Figure 2 (to be Figure 9 in revised manuscript). Scatter plot of dissolved oxygen (DO) and pH at 7 m (grey hatches) and 17 m (purple hatches) water depth from all SeapHox deployments from 10 July, 2010 – 19 October, 2011. Dashed black line is the linear relationship between pH and DO for all data regardless of depth. Solid black line represents expected changes in DO and pH with production and respiration (P:R) at present-day conditions (384 ppm CO$_2$). Future changes in pH due to ocean acidification are modelled at oxygen saturation and CO$_2$ levels of 800 ppm (OA; dashed red line) along with the corresponding changes in the P:R relationship (solid red line).

**References**


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Melzner, F., Thomsen, J., Koeve, W., Oschlies, A., Gutowska, M. A., Bange, H. W., Hansen, H. P., Körztzinger, A.: Future ocean acidification will be amplified by hypoxia in


Fig. 1. See figure caption above.

Fig. 2. See figure caption above.