Overall author response: We thank the reviewers and associate editor for careful consideration of our manuscript. We address all reviewer comments below, which for ease, we have copied. Original reviewer comments are in Arial font and author responses are in Times New Roman italicized.

- 5
- Interactive comment on "A year in the life of a central California kelp forest: physical and biological insights into biogeochemical

variability" by David A. Koweek et al. Anonymous Referee #1

10 Received and published: 4 October 2016

General Comments:

This study presents 1+ year time-series data of weekly samples of carbonate chemistry across a small spatial scale of a kelp forest covering two summer seasons. The data include surface and bottom samples in exposed and protected sites and from inside to outside the kelp forest. The data are of extremely high quality. The

15 paper is well written, articulate, and has logical organization with nice transitions. While carbonate chemistry time series papers are increasing in number, this paper contributes novel and valuable data on small scale spatial variability (depth and spatial). In support of publishing this paper, I consider my comments as minor revisions which would improve the scientific quality from 'good' to 'excellent'.

20 Thank you for your thoughtful comments and careful review of this paper. We address your specific comments below.

Specific Comments:

I have three specific comments, two with regard to the spatial variability. First, bottom water sampled by site is confounded by depth, which is not explicitly addressed. The spatial variation of bottom water could just be an

- 25 artifact of the stratification of the water column within which the kelp forest sits (deeper waters have more DIC, so therefore bottom waters of deeper sites will have lower DIC values than bottom waters of shallower sites). The potential depth dependency of the observed dynamics (and conclusions) should be addressed and contextualized with the aims of the study (and the sampling design of surface and bottom waters, which was not explained). The data are valuable in terms of understanding the variation of what, for instance, a benthic
- 30 kelp forest inhabitant might experience, but then that perspective should be included (Introduction and Discussion).

We agree that bottom water sample variability is confounded by depth variability. Sections 3.4 and 3.5 already address the role of depth in establishing bottom water carbon system variability. Section 4.1 ("Mechanisms of observed variability") has been edited to include more text and explicit discussion of the role of depth variability in shaping the observed spatial

35 patterns in carbonate chemistry. However, as we also discuss in Section 4.1, differences in bottom water exchange between



the protected and exposed sides (as measured by ADCPs at similar depths), suggest additional localized factors that contribute to spatial variability. Finally, we have added a sentence to Section 2.2 to provide context for the sampling depths we chose in this study.

- 5 Second, the most valuable portions of this study are the depth gradient (well developed and presented) and the spatial gradient of the time-series (from inside to outside a kelp forest, exposed to protected). The presentation of the latter (Section 3.5) is extremely short and the figures comprise mostly of statistical numbers and not meaningful observations. The authors do themselves a disservice by not highlighting this aspect of the study more in depth. Figures 9 and 10 do not contribute anything that could not be shown in a
- 10 table (Fig. 9b, 8, and S8 display duplicate data in every plot). Fig. 9a could be interesting if shown as a line graph (bar graph is too cluttering) but I don't think it's necessary in the first place. Instead, I was expecting a figure showing the gradient in carbonate chemistry from inside to outside the kelp forest at the two contrasting sites (protected, exposed). How does these gradient change by season? It looks like the largest spatial differences occur between the exposed vs. protected site and not within the inside vs. outside (I
- 15 suspect that differences between inside and outside kelp forest will only be apparent with higher frequency sampling). The statistics show this, but the figure space would be better used by using the real data (e.g. select parts of the time-series, moving averages, etc.).

We reorganized Figure 9. Figure 9b in the Biogeosciences Discussion paper is now Fig. 9a, which helps highlight the clustering of the Pro Inn and Pro Mid sites relative to the other four sites. Figure 9a in the Biogeosciences Discussion paper

- 20 is now Fig. 9b and has been modified to show the histogram of aragonite saturation state observations for two groupings: Pro Inn + Pro Mid and the other four sites. Grouping the data into two sets helps better illustrate the spatial differences between Pro Inn and Pro Mid relative to the four deeper sites. We added additional text to Section 3.5 to better complement the new Figs. 9a and 9b, as well as to better clarify the unique and complementary contributions of Figs. 9 and 10. Specifically, Fig. 9 shows differences in average bottom conditions, whereas Fig. 10 shows differences in bottom co-
- 25 variation between sites.

Lastly, the Discussion is largely devoted to the value of time-series, this could probably be condensed. As an edition, the results should be discussed in terms in the context of other studies of kelp forest or coastal variability in general (some were mentioned in the Introduction). Do these data fall within the range of biochemical observations made previously in other kelp forests?

We have added several sentences to the beginning of the Discussion section to contextualize our results by comparing our pH range to that of the southern California studies listed in the Introduction.

2

Other and Technical Comments:

35

Shorten the LPJPSMR acronym

We have removed this acronym

2.1 L23: of kelp of the kelp

5 We corrected this error

2.4 L6: provide reason or reference for phosphate assumption

We made phosphate measurements from February-August 2014. We have edited the sentence in question to let readers know that these measurements were made during the study and we refer them to the attached data file for the original measurements.

2.4 L8: pHT is defined but not used in subsequent reporting of pH values in the Results.

We removed references to pH_T

15 2.4 L11: double))

10

The double)) was used because the reference was cited within a parenthetical statement. We replaced the inside set of parenthesis with brackets for the reference inside of the parenthetical statement.

For all time series figures: simplify x-axis date labels. Adding 01 as the day is not

20 necessary and adds clutter. I recommend to simply label months as 1-12.

We have simplified the x-axis labels on all time series plots to show only the month number.

3.2 L23: "causing water column temperature differences of up to 4_C" add across what range of depths

25 We added the depth of the Protected Offshore site in this sentence

3.3 L 16-17: "Surface DIC concentrations were generally much more spatially homogeneous than bottom water DIC concentrations." Could just be function of depth.

We agree that much (but not all) of the bottom DIC differences can be attributed to depth. We still think that much of the

30 surface homogeneity is due to the strong biological influence in the surface waters, as we discuss in the Discussion section.

3.3 L25: has should be had

We corrected this error

35 3.3 L27: regarding pCO2 undersaturation, add "with respect to the atmosphere" if that

is what you are measuring saturation against.

We added this clause

5

Table 2: Since bottom depth differs across sites (7.5-16 m) and there are obvious depth

effects, add the depth in m in () following the listed value in Table 2.

Depths for all study sites are already listed in Table 1

3.4 L21: "drove large variations in the ability to buffer against ongoing ocean acidification".

Ocean acidification is not detectable across such a short time-series. Reword to simply say, "drove large 10 variations in the Revelle Factor".

We replaced the sentence with the reviewer's suggested sentence

3.5: Why was aragonite used here (and not TA or DIC)?

We chose to use the aragonite saturation state because we thought this carbonate system parameter would be more familiar and more easily comprehendible to a broad suite of scientists working on ocean acidification and global change. We note that section 3.4 establishes that DIC variability is the dominant driver of observed variability in aragonite saturation state.

4.1 L28: Regarding this paragraph, it would be nice if you could find a reference showing the seasonality of phytoplankton blooms of this site. I imagine it is offset from the

20 kelp forest growing season.

This would be a nice addition, but we do not have the data. As we identify in the Discussion section, this is a hypothesis for future work and points to the need to have an offshore control site against which to compare the nearshore biogeochemical variability.

- 25 4.2 L22 State the actual findings. The largest source of variation seems to be the protected vs. unprotected sites, which is actually a function of the oceanographic features, not a function of the biology of the kelp forest. The biological control is in this study is the depth gradient (where primary production takes up DIC at the surface).
- We hypothesize that oceanographic processes control the bottom waters, but that biological processes control the surface waters (at least during periods of high primary production). We discuss this hypothesis, along with the supporting observations, in Section 4.1. The paragraph that you reference serves as a starting point for discussing the implications of the work. Further discussion of the mechanisms behind the observed variability would be redundant from the previous section.
- 35 Pg. 11 L9: inconsistent use of OA vs. ocean acidification. I recommend to not use the

acronym at all.

We have removed all uses of 'OA' and replaced with 'ocean acidification'

Pg 11, L10: other studies have shown this previously also: pH sensor-based studies

5 $\,$ in coastal environments but also cruise data for offshore regions. Cite references in

support of this conclusion.

We respectfully disagree with the comment to include offshore references. This study is explicitly about a nearshore ecosystem. We already openly acknowledge the limitations of not having offshore data in our study. Discussing other's offshore observations of primary production is outside the scope of this manuscript.

10

Pg. 11 L13: The ocean is not acidic, acidifying and acidic are different.

We replaced with 'acidifying'.

Pg. 11 L16: Same as previous comment. It makes more sense to use 'low pH' instead

15 of 'high acidity'

We replaced 'high acidity' with 'low pH'

Interactive comment on "A year in the life of a central California kelp forest: physical and

20 biological insights into biogeochemical variability" by David A. Koweek et al.

Anonymous Referee #2

Received and published: 10 October 2016

This manuscript nicely describes spatial and temporal variation in carbon system variables in a kelp forest in Central California. The data presented are the first to report high frequency measurements of carbon system

25 variables made at small spatial scales across an entire annual cycle within a kelp forest. The data reveal substantial depth-dependent, spatial, and seasonal differences. The authors suggest mechanisms that could be responsible for creating the observed variation. Sampling design, sample collection, and analytical methods all appear appropriate to the research questions posed. The organization of the paper is logical, the writing is clear, and the graphics are appropriate and informative. Below I offer specific comments intended to

30 strengthen the manuscript.

Thank you for your thorough and considerate review of this paper. We address your specific comments below.

Page 2, line 8: more clearly stated as "Calcification and dissolution of kelp-associated organisms, especially shelled invertebrates, can modify water chemistry..."



The sentence now reads: "Calcification and dissolution of kelp-associated organisms, especially shelled invertebrates, modify the water chemistry through the uptake and release of carbonate and bicarbonate ions, which modify the total alkalinity (TA) and DIC."

5 Page 2, line 16: better stated as " Despite the recognized importance of the kelp forest. . ."

Opening clause in the paragraph now reads as "Despite the recognized importance of kelp as a foundation species and biogeochemical agent,..."

Page 2, line 16: I searched but did not find reference to kelp as an "ecosystem architect". The earlier use of the 10 term "foundation species" is more consistent with the ecological literature.

We replaced "ecosystem architect" with "foundation species"

Page 2, lines 25-27: Important points are made here. It would be helpful to clearly return to these in the discussion section.

15 We have added text to the opening sentence of section 4.2 to more clearly indicate our return to these discussion points.

Section 2.4 Satellite derived estimates: Estimating kelp canopy biomass is notoriously difficult. The authors have done a good job estimating relative changes in biomass over time but I found no indication in the text or figures to indicate error in this estimate. The inclusion of error estimates would be helpful.

- 20 We added text to Section 2.5 (was incorrectly labelled as Section 2.4 earlier) to describe the error estimation procedure for the kelp canopy biomass estimates. Figure 2a now shows the 95% confidence interval around the kelp canopy biomass estimates.
- Section 3.4: Carbon systems variables differ between surface and bottom, consistent with the intrusion of CO2 enriched water at bottom and photosynthetic activity at the surface. Here or in the discussion it could be helpful to mention that the observed surface-to-bottom variation suggests that benthic calcifiers appear neither to be influencing TA nor do they appear to be benefitting from the effects of photosynthesis on water chemistry, which seem to be confined to surface waters. Moreover, understory seaweeds, which can achieve substantial biomass in kelp forests, don't appear to affect water chemistry appreciably (tho this was not tested). A fuller discussion of these considerations could be helpful.

We expanded section 4.1: 'Mechanisms of observed variability' to include a brief discussion of how we do not see strong evidence for calcification, as inferred from the TA data, and that understory production may be an important process, but we do not have the vertical sampling resolution to quantify the role of understory production in the observed biogeochemical gradients.

Section 4.2: The discussion of "space-for-time substitutions" is reasonable, but in my opinion is less compelling than other arguments that can be made concerning kelp forest ecosystems in an era of global change. I'd encourage the authors to open the discussion with the most compelling inferences that can be drawn from their data.

- 5 We respectfully disagree with the reviewer on this point. We believe that the most impactful results from our study point to the importance of considering small-scale spatial variability in kelp forests. Small-scale spatial variability potentially creates differential organismal responses to local conditions, which may then scale to create observed ecosystem-level responses to environmental conditions. Therefore, understanding the organismal response to small-scale variability is critical to predicting the ecosystem response. The variations in DIC create opportunities for looking at how organismal
- 10 responses differ between high and low DIC regions of the kelp forest. This "space-for-time" approach encompasses observational and manipulative work that will help build our understanding from small-scale spatial variability to organismal response to ecosystem response.
- Page 11, lines 10-18: The discussion of refugia could be refined. Assuming that photosynthesis within the canopy modulates stress due to high CO2/low pH, it's difficult to think of very many organisms (especially calcifying organisms) that can take advantage of this. These are likely to be limited to epibionts on kelp blades and perhaps a few canopy-associated fish species. A much larger number of calcifying taxa are associated with the benthos, where water conditions are likely to be less conducive to calcification and growth when omega is low. Consequently, the potential refugium created by the canopy is spatially unassociated with the 20 bulk of benthic species. Moreover, the persistence of refugia in such a dynamic system is questionable.
- We agree that benthic organisms are unlikely to benefit from any biogeochemical refugia created by the photosynthetic activity in the kelp canopy. However, our results point to consistent vertical biogeochemical gradients during times of high kelp biomass. Therefore, any mobile organisms sensitive to high CO_2 may increasingly find refuge in the surface waters. Testing this idea is beyond the scope of our paper (and we don't have any data with which to do so). However, we believe it
- 25 is important to mention this hypothesis in the Discussion section so that others can use our data as motivation to more formally test for the presence and importance of biogeochemical refugia in such dynamic systems.

Page 11, lines 25-34: Comments about water quality criteria are reasonable: for instance, it's important to point out that the variability observed in this study exceeds that of water quality criteria now in existence. However, the paragraph doesn't seem particularly nuanced, beyond references to Boehm et al, Weisberg et al, and Chan

30

et al. I encourage the authors to more fully consider the implications of their data for water quality criteria. We use this paragraph to compare our observations to existing water quality regulations. However, we believe that an extensive review of water quality regulations along the west coast of North America, and how they interact with biogeochemical variability in a kelp forest, is beyond the scope of this paper. Extensive additions to this section of the paper

would further extend the Discussion section of the paper. Reviewer #1 already suggests reducing the length of the Discussion and we believe further lengthening would take focus away from the main scientific points of the paper.

Page 11, line 28: replace "supervising agencies" with "regulatory agencies".

5 We replaced "supervising agencies" with "regulatory agencies"

Page 12, line 8: distinguish between "fully constrained" and "over-constrained" with respect to carbon system variables.

Thank you for identifying this subtle, but very important, difference. We revised this sentence to emphasize the crucial

10 importance of fully constraining the carbonate system (measuring 2 carbonate system parameters), with a goal of overconstraining the carbonate system (measuring 3 or more carbonate system parameters).

8

Page 12, line 18: replace "harvesting" with "kelp harvesting".

We replaced "harvesting" with "kelp harvesting"

15

Page 12, line 20: should read "effects of the kelp canopy".

We now use "effects of the kelp canopy"

Page 12, line 22: replace "chemically homogenize" with "reduce gradients in".

20 We replaced "chemically homogenize" with "reduce gradients in"

A year in the life of a central California kelp forest: physical and biological insights into biogeochemical variability

David A. Koweek^{1,*}, Kerry J. Nickols^{2,3}, Paul R. Leary², Steve Y. Litvin², Tom W. Bell⁴, Timothy Luthin¹, Sarah Lummis^{2,#}, David A. Mucciarone¹, and Robert B. Dunbar¹

Correspondence to: David A. Koweek (dkoweek@carnegiescience.edu)

15 Abstract.

95060, USA

Kelp forests are among the world's most productive marine ecosystems, yet little is known about their biogeochemistry. This study presents a fourteen-month time series (July 2013-August 2014) of surface and benthic dissolved inorganic carbon and total alkalinity measurements, along with accompanying hydrographic measurements, from six locations within a central California kelp forest. We present ranges and patterns of variability in carbonate chemistry, including pH (7.70-8.33), pCO₂

- 20 (172-952 μ atm), and the aragonite saturation state, Ω_{Ar} (0.94-3.91). Surface-to-bottom gradients in CO₂ system chemistry were as large as the spatial gradients throughout the bottom of the kelp forest. Dissolved inorganic carbon variability was the main driver of the observed CO₂ system variability. The majority of spatial variability in the kelp forest can be explained by advection of cold, dense high CO₂ waters into the bottom of the kelp forest, with deeper sites experiencing high CO₂ conditions more frequently. Despite the strong imprint of advection on the biogeochemical variability of the kelp forest,
- 25 surface waters were undersaturated with CO₂ in the spring through fall, indicative of the strong role of photosynthesis on biogeochemical variability. We emphasize the importance of spatially distributed measurements for developing a processbased understanding of kelp forest ecosystem function in a changing climate.

1. Introduction

Kelp forests are found along rocky coastlines in temperate-to-sub-polar coastal regions throughout the world's oceans. Kelp are important foundation species that support diverse biological communities, including invertebrates, fishes, and marine mammals through their creation of complex, three-dimensional biological habitat and the provisioning of carbon and nutrients which magnify secondary production in the coastal zone (Steneck et al., 2002). Kelp forest ecology has been a

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focus of study since the early twentieth century, largely due to its importance as an ecologically rich habitat (as reviewed in Graham et al. 2007).

Kelp (including *Ecklonia spp., Laminaria spp., and Macrocystis spp.*) forests are among the most productive marine ecosystems (Mann, 1982), with linear extension rates of kelp fronds that can range from 2-14 cm d⁻¹ (Graham et al., 2007).

- 5 Productivity rates vary depending upon the geographic region and species of consideration, but generally range from 600-1500 g C m⁻² yr⁻¹ (Mann, 1982), although they have been documented to reach up to 3400 g C m⁻² yr⁻¹ (Jackson, 1977). The high productivity in kelp forests impacts the chemical properties of the surrounding water through the uptake and release of dissolved inorganic carbon (DIC) and dissolved nutrients (nitrate and phosphate). Calcification and dissolution <u>of kelp-associated organisms</u>, especially shelled invertebrates, modify the water chemistry through the uptake and release of
- 10 carbonate and bicarbonate ions, which modify the total alkalinity (TA) and DIC. Air/sea gas exchange further modifies the DIC through exchange of CO₂. In addition, in the upwelling zones that support kelp forests, carbon system chemistry undergoes large fluctuations due to highly dynamic regional-scale advection of high CO₂ deep waters (Booth et al., 2012). The combination of biological and physical processes can lead to large biogeochemical variability in kelp forests. For example, pH (NBS scale) values of up to 9.1 have been recorded in one sub-Antarctic kelp forest while matching samples
- taken directly outside the kelp bed had pH (NBS scale) of 8.3 (Delille et al., 2000). In southern California, Frieder et al. (2012) measured pH (total scale) values as low as 7.7 (corresponding to pCO₂ of 1000 µatm).

Despite the recognized importance of kelp as a foundation species and biogeochemical agent, little attention has been paid to biogeochemical variability in kelp forests (see Delille et al., 2000, 2009; Frieder et al., 2012; Hofmann et al., 2011; Kapsenberg and Hofmann, 2016; Takeshita et al., 2015). Of the few studies that have addressed kelp forest

- 20 biogeochemistry, most have focused on pH measurements in southern California (Frieder et al., 2012; Hofmann et al., 2011; Kapsenberg and Hofmann, 2016; Takeshita et al., 2015), which while certainly useful, does not provide complete information about the CO₂ system chemistry in kelp forests. The lack of geographically distributed biogeochemical observations in kelp forests may be due to the difficulties of long-term field observations and/or the lack of automated instrumentation and procedures for making continuous, high-quality biogeochemical measurements until recently
- 25 (Bresnahan et al., 2014). Our limited understanding of kelp forest CO₂ system chemistry inhibits our ability to establish biogeochemical baselines as well as to forecast how kelp forest communities may interact with changes in water chemistry from local stressors, such as runoff and sedimentation, as well as from global stressors, such as climate change and ocean acidification (OA).
- The genus *Macrocystis* (order Laminariales), or giant kelp, is the most widely distributed kelp genus in the world. 30 Found in both the northern and southern hemispheres, it dominates kelp assemblages in southern and central California (Graham et al., 2007). We present results from a 14-month biogeochemical study in a central California *Macrocystis pyrifera*-dominated kelp forest. Our goals were to quantify temporal and spatial carbon system biogeochemical variability in a kelp forest over an annual cycle and investigate the responsible mechanisms.

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2. Methods

2.1 Study Site

Our study site is located along the eastern side of the Monterey Peninsula in the central portion of the California Current Large Marine Ecosystem (Fig. 1) (Checkley and Barth, 2009). This region is characterized by seasonal upwelling

- conditions driven by increased northwesterly winds from ~March-September (Checkley and Barth, 2009) (Fig. S1). 5 Although much of the Monterey Peninsula is protected from the stronger along shore winds and associated surface conditions experienced by the nearby exposed coastline and northern Monterey Bay, it still experiences cross-shore transport associated with upwelling (Woodson, 2013). Advection of upwelled waters and the local topography also facilitate the propagation of internal bores into southern Monterey Bay, which act as an additional mechanism for introducing dense, high
- CO2 deep ocean water into nearshore habitats and driving variability in CO2 chemistry at short temporal scales (Booth et al., 10 2012; Walter et al., 2014).

The kelp forest is located in the Lovers Point-Julia Platt State Marine Reserve, directly offshore of Hopkins Marine Station along the wave-protected side of the Monterey Peninsula (Fig. 1). The reserve was created in 2007 as part of the network of central California marine protected areas designated under the California Marine Life Protection Act (California

15 Department of Fish and Wildlife 2016). The kelp forest in the Lovers Point-Julia Platt State Marine Reserve, has been protected since 1931, originally as the Hopkins Marine Life Refuge. Due to its protected status, the reserve serves as a natural laboratory to investigate the biogeochemistry of a central California kelp forest featuring low levels of human disturbance.

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Within this kelp forest we selected six sites that span gradients in wave exposure, depth, and proximity to the kelp 20 bed (Fig. 1; referenced as Protected Inside, Protected Middle, Protected Offshore, Exposed Middle, Exposed Offshore, and KFA). Sites inside the kelp bed ranged from 7.5-11 m and sites just outside the kelp bed ranged from 13.5-16 m depth. The site inside the kelp bed on the wave-exposed side (Exposed Middle) was slightly deeper than sites on the protected side because we were unable to reliably sample the wave-exposed side of the kelp bed in shallower waters for operational reasons. The six sites ranged from 130-270 m offshore (Table 1). Sites along the transect on the western side of the kelp 25 forest experienced greater wave exposure than sites on the protected side due to the northwestern directionality of incoming waves (Fig. S2). Both the wave-exposed and wave-protected transects were oriented perpendicular to the kelp forest in order

to sample within and just outside of the kelp bed. The KFA site (located above the main node of the Kelp Forest Array, an underwater cabled observatory) was located east of the protected transect and served as a kelp-free control site, although it was close enough to the kelp forest to be influenced by the advection of chemically-modified water from the kelp forest.

2.2 Water Sampling

We sampled biogeochemical and hydrographic properties at the six study sites at approximately weekly intervals spanning July 2013-August 2014. Samples were collected between 0900 and 1200 hrs in order to minimize any potential confounding influence of the diel cycle on the weekly-scale biogeochemical variability. We collected water samples for DIC

- and TA analysis at 1 m below the surface (1 mbs) and 1 m above the bottom (1 mab) using 1.7L Niskin bottles at all 6 sites
 (Fig 1). We chose these depths for water sampling in order to sample where most of the kelp biomass resided (1 mbs) and where most kelp forest inhabitants lived (1 mab). Water was sampled from the Niskin bottle into a 30mL bottle for DIC and a 300mL bottle for TA. Samples were immediately preserved by addition of 30 µL (DIC) or 300 µL (TA) saturated mercuric chloride solution (HgCl₂) upon collection from Niskin bottles. Samples were typically analyzed within 1-2 weeks of collection. We conducted simultaneous CTD hydrocasts (SBE 19plus, SeaBird Electronics, Inc.) at each station to
- characterize the vertical water column structure and provide *in-situ* temperature and salinity necessary for carbon system calculations (see below).

We used CTD hydrocasts to quantify water column stratification by determining the density difference the between the upper two meters and the bottom two meters.

(1)

$$\Delta
ho =
ho_{bottom} -
ho_{surface}$$

where $\Delta \rho$ is in kg m⁻³, $\overline{\rho}_{bottom}$ is the average density across the bottom two meters of the water column, and $\rho_{surface}$ is the average density across the top two meters of the water column. We chose to average across two meters at both the top and bottom sites in order to span the depth of water sample collection (1 mbs and 1 mab).

Sample sets from July and August 2013 were collected over two days, with the samples from the protected transect 20 typically collected a day before the samples from the exposed transect and the KFA site. We include these first two months of the time series when presenting the data as time series, but in order to avoid confounding variability from sampling on different days, any of the analyses presented here which require comparisons between the sites are limited to the period of September 2013-August 2014 when samples were all collected within approximately 90 minutes of one another.

2.3 Water chemistry

15

Water samples were analyzed at the Stanford University Stable Isotope Biogeochemistry Laboratory (Stanford, California, USA). DIC was measured with a custom-built sample acidification and delivery system coupled to an infrared gas analyzer (Licor 7000) described in Long et al. (2011). The instrument was calibrated prior to each use and monitored throughout run sequences with Certified Reference Materials (CRM) provided by A. Dickson (Scripps Institution of Oceanography). Instrumental precision from 467 CRM analyses over the length of the study was ±1.9 µmol kg⁻¹ (1 S.D.).
 Immediate duplicate analyses of samples usually yielded instrumental precision of 1-2 µmol kg⁻¹.

Samples for TA measurements were pre-filtered through a 0.45 µm filter before being analyzed on a Metrohm 855 Robotic Titrosampler (Metrohm USA, Inc.) using certified 0.1N HCl provided by A. Dickson (Scripps Institution of Oceanography). Total alkalinity calculations from raw titration data follow Dickson et al. (2003). Sample runs were corrected based on the offset between the measured and certified value for CRMs, resulting in an accuracy that was always

5 better than 1.7% and was better than 0.5% on 79% of analyses. Instrumental precision from 272 CRM analyses over the duration of this study was ±2.2 µmol kg⁻¹ (1 S.D.). Immediate duplicate analyses of samples usually yielded instrumental precision of 1-2 µmol kg⁻¹.

2.4 Carbon system calculations

We calculated pH, pCO₂, and Ω_{Aragonite} (Ω_{Ar}) in CO2SYS (van Heuven et al., 2011) using DIC, TA, *in-situ*temperature, and salinity data. We assumed silica concentrations of 3 µmol kg⁻¹ (Brzezinski et al., 2003) and phosphate
concentrations of 0.5 µmol kg⁻¹ and 1 µmol kg⁻¹ for the surface and bottom, respectively, <u>based on measurements made in</u>
<u>February-August 2014 (see attached data file for original data)</u>. We used the carbonate system dissociation constants from Mehrbach et al. (1973) as re-fit by Dickson and Millero (1987), and K_{SO4} for the bisulfate ion from Dickson (1990). pH data is reported here on the total hydrogen ion scale at in-situ temperature.

15

We estimated error for pH, pCO₂, and Ω_{Ar} calculations using a Monte Carlo approach. We randomly selected ten samples in the data set, used the above-listed instrumental precisions for DIC and TA, assumed no error on the temperature and salinity measurements, and performed 1000 iterations on each of the ten samples. We did not consider error on the carbonate system equilibrium constants. The Monte Carlo simulations resulted in simulated distributions of pH, pCO₂, and Ω_{Ar} for each of the ten randomly selected samples in the data set. We calculated the standard deviation of each distribution.

20 The maximum standard deviation of the set of ten simulated distributions of pH, pCO₂, and Ω_{Ar} are 0.01 units, 20 µatm, and, 0.03 units, respectively. We consider these error estimates to be conservative since they are the maximum, instead of average, values.

We quantified the effects of TA, DIC, temperature, and salinity on the observed vertical differences ($\Delta y_{Top-Bottom}$) in pH, pCO₂, and Ω_{Ar} , using a first order Taylor series budget following Hauri et al. (2013):

25
$$\Delta y_{_{Tep-Bottom}} = \frac{\partial y}{\partial T} \Delta T_{T-B} + \frac{\partial y}{\partial S} \Delta S_{T-B} + \frac{\partial y}{\partial TA} \Delta TA_{T-B} + \frac{\partial y}{\partial DIC} \Delta DIC_{T-B}$$
(2)

where *y* is pH, pCO₂, or Ω_{Ar} and the terms on the right-hand-side of the equation account for the effects of temperature, salinity, TA, and DIC, respectively. The partial derivatives $(\frac{\partial y}{\partial T}, \frac{\partial y}{\partial S}, \frac{\partial y}{\partial TA}, \frac{\partial y}{\partial DIC})$ were estimated numerically in CO2SYS centered at the mean values of temperature, salinity, TA, and DIC across the entire data set (Table S1).

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2.5 Satellite-derived kelp canopy biomass estimates

We estimated giant kelp canopy biomass from July 2013 to August 2014 using multispectral Landsat 7 Enhanced Thematic Mapper and Landsat 8 Operational Land Imager imagery (Bell et al., 2015a; Cavanaugh et al., 2011). Briefly, each Landsat image was atmospherically corrected using 50 temporally stable pseudo-invariant targets to standardize radiometric

5 signals across dates. The proportion of kelp canopy in each 30m x 30m pixel was determined using multiple end-member spectral mixing analysis (Roberts et al., 1998), in which each pixel was modeled as a combination of 1 static kelp end-member and 30 seawater end-members, which were unique to each image. Kelp canopy biomass and 95% confidence intervals were estimated by comparing diver estimated canopy biomass and Landsat pixel kelp fraction using a reduced major axis linear regression (MATLAB function lsqfitgm; detailed methods in Cavanaugh et al. [2011]).

10 2.6 Current velocity time series

Water-column velocity was measured continuously near the exposed and protected sites in the middle of the kelp forest using bottom-mounted Acoustic Doppler Current Profilers (RD Instruments, 1200 kHz). The instruments recorded ensemble averaged velocities every 3 minutes in 0.5 m bins extending from ~1.5 m above the bottom to ~1.5 m below the surface. The instrument on the protected side of the kelp forest was deployed through December 2013.

3. Results

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3.1 Kelp canopy biomass

Satellite-estimated kelp canopy biomass displayed a strong seasonal cycle, consistent with previous observations of the strong seasonality of kelp canopy biomass in central California (Bell et al., 2015b; Reed et al., 2011). Canopy biomass 20 increased throughout spring, reached a maximum during the summer months, and decreased throughout the fall, reaching minimum values in the winter. The timing of kelp growth, senescence, and canopy biomass range were generally consistent between the wave-protected and wave-exposed sides of the kelp forest (Fig. 2a). However, canopy biomass on the exposed side began to decline slightly before canopy biomass on the protected side in summer 2014, leading to a decoupling of canopy biomass between the two sides from June-September 2014.

25 3.2 Water column structure

The kelp forest water column was strongly influenced by seasonal variations in surface and bottom water temperature. We use the protected side transect, which spans the largest range in site depths, to examine these processes in detail (Fig. 3). During the spring, cold (~10°C), dense bottom water was advected into the deepest kelp forest site (Protected

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Deleted: Kelp canopy biomass was estimated using the observed relationship between diver estimated canopy biomass and Landsat pixel kelp fraction in the Santa Barbara Channel (where this technique was originally applied-see David Koweek 11/28/2016 12:14 PM Deleted: (David Koweek 11/28/2016 12:14 PM Deleted:) David Koweek 12/12/2016 12:09 PM Deleted: 4 Offshore), causing water column temperature differences of up to 4°C_across 16 meters depth. This cold bottom water did not reach further inshore along the bottom of the shallower, inwards Protected Middle and Protected Inside sites (Fig. 3). Surface heating during summer 2014 resulted in uniformly warm surface waters (~16-18°C) across the sites along the protected transect. Reduced stratification at the shallower Protected Inside site allowed warmer surface waters to mix

5 downwards, which resulted in a nearly isothermal water column whereas temperature stratification was maintained in the deeper Protected Offshore site. Salinity showed a seasonal cycle across all three sites of the protected transect with higher salinity during upwelling season, where values ranged from ~33.6-34, as compared to less saline winter months, where salinity ranged from 33-33.6 (Fig. S3). However, there was little evidence for depth-dependent variation in salinity, suggesting that temperature was the dominant control on water column stratification. These patterns were similar across all sites.

Water column stratification, as quantified by $\Delta \rho$, was greatest and most variable from the start of upwelling season throughout the fall where $\Delta \rho$ exceeded 1 kg m⁻³, with strong site-to-site variability (e.g., June-August 2014; Fig. 2b). Throughout most of the year, $\Delta \rho$ was greatest and most variable at the Protected Offshore, KFA, Exposed Offshore, and Exposed Mid sites. Protected Middle and Protected Inside typically, although not always, had lower $\Delta \rho$ and less variability from week-to-week. All sites were minimally stratified in the winter months, as $\Delta \rho$ generally stayed below 0.4 kg m⁻³ and was generally less than 0.2 kg m⁻³ in December 2013-February 2014. Site-to-site variability was also reduced in the winter months, although there was one anomalously high stratification observation at the Exposed Offshore site in early January 2014, where $\Delta \rho$ nearly reached 1 kg m⁻³.

3.3 CO₂ system chemistry time series

- The 14-month time series of DIC for all six sites near the surface (1 m below sea level) and the bottom (1 m above the sea floor) exhibited strong week-to-week, site-to-site, and seasonal variability (Fig. 4a). Bottom DIC frequently exceeded 2100 µmol kg⁻¹ during Fall 2013 and exceeded 2200 µmol kg⁻¹ at all sites except Protected Middle during April-May 2014.
 The <u>four deepest sites typically had highest bottom DIC during the spring and summer months, although the site-to-site variability disappeared during the winter. Surface DIC concentrations were generally much more spatially homogeneous
 </u>
- 25 than bottom water DIC concentrations. Surface DIC reached minimum values during spring and summer months when DIC was frequently less than 2000 μmol kg⁻¹.

The time series of surface and bottom TA shows reduced variability compared to the DIC time series (Fig. 4b). Surface and bottom TA samples generally ranged from 2240 to 2260 µmol kg⁻¹, with occasional higher values observed. Unlike DIC, TA did, not show any consistent surface-to-bottom gradients throughout the time series. Increased TA during the

30 upwelling season was likely due to the high nutrient content of the source waters being advected into the kelp forest.

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David Koweek 11/30/2016 3:44 PM Deleted: oes Time series of pH, pCO₂, and Ω_{Ar} all exhibited similar properties to the DIC time series with strong week-to-week, site-to-site, and seasonal variability (Fig. 5). Minimum pH values in bottom samples ranged from 7.70-7.79 across the six sites, and pH minima grouped closely to site depth, where the four deeper sites had pH minima which ranged from 7.70-7.79, while the pH minima at Protected Middle was 7.78 and the pH minima at Protected Inside was 7.79 (Fig. 5a). Bottom

5 Ω_{Ar} values exhibited similar clustering as pH. Surface pCO₂ was undersaturated with respect to the atmosphere (<400 µatm) through the early fall, spring, and summer, although week-to-week variability resulted in periods of pCO₂ saturation and supersaturation during July and August 2014 (Fig. 5b). We observed Ω_{Ar} undersaturation (Ω_{Ar} <1) five times: at Protected Offshore on 25 April 2014 and 14 May 2014 and at KFA, Exposed Offshore, and Exposed Middle on 14 May 2014. Table 2 provides a summary of all carbon system variable ranges.

10 3.4 Surface-to-bottom variability

The combination of maximum kelp abundance and water column stratification led to greatest carbon system variability within the kelp forest during the upwelling season (~March-September). Ranges in DIC along the top, along the bottom, and vertical gradients at each sampling site, exceeded 100 μ mol kg⁻¹ at this time (Fig. 6a). Winter mixing from storms and the lack of kelp canopy reduced these differences, resulting in chemical gradients which approached 0 μ mol kg⁻¹.

15 TA spatial variability was much smaller and more variable (Fig. 6b). pH, pCO₂, and Ω_{Ar} exhibited strong top to bottom differences as well. Vertical differences in pH and Ω_{Ar} reached up to 0.51 and 2.25 units, respectively.

Nearly all of the surface-to-bottom variability in pH, pCO₂ and Ω_{Ar} can be attributed to vertical differences in DIC using Eq. (2). The DIC contribution to the observed surface-to-bottom differences in pH, pCO₂ and Ω_{Ar} across the six sites ranged from 88-93%, 82-88%, and 92-97%, respectively (Fig. 7 and S4-6). These results are consistent with an ecosystem
 dominated by organic carbon metabolism (photosynthesis/respiration) as opposed to inorganic carbon metabolism

(calcification/dissolution), an expected result in a kelp forest. We note that the carbon system budgets do not discriminate between local biogeochemical modification within the kelp forest and advection of offshore water.

Cold, high DIC water observed at the bottom of the kelp forest was a major contributor to surface-to-bottom differences in DIC (Fig. 8). High DIC water reached the deeper sites (Protected Offshore, KFA, Exposed Offshore, Exposed

25 Middle), but did not frequently penetrate into the shallower sites (Protected Middle and Protected Inside). Bottom DIC accounted for 55-67% (pearson correlation coefficients) of observed surface-to-bottom DIC gradients in the four deeper sites (Fig. 8b), but only accounted for 39% of the observed gradient at Protected Middle and 22% of the gradient at Protected Inside. Reduced stratification at the protected shallower sites reduced water column temperature and DIC gradients (Figs. 2b, 3, and 4).

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The vertical variability in CO₂ system chemistry drove large variations in the <u>Revelle Factor</u>. The Revelle Factor describes the non-linear buffering capacity of seawater $RF = \partial \ln pCO_2 / \partial \ln DIC$. Higher *RFs* indicate reduced capacity to buffer against increasing CO₂ as ocean acidification progresses. *RF* variability within the kelp forest ranged from ~9-18

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over the annual cycle (Fig. S7), which nearly spans the range of global surface ocean values from offshore waters (Sabine et al., 2004). Following other carbon system properties, the highest and most variable RFs were observed in the bottom waters during spring and summer. Photosynthetic uptake in the surface during upwelling months lowered RFs to between 10-12, with occasional values reaching below 10. Winter RFs for surface and bottom water samples converged around 12-14.

5 3.5 Spatial Variability

Full-year histograms of Ω_{Ar} in kelp forest bottom waters revealed significant differences (Wilcoxon rank sum test, α =0.05) between the sites generally according to site depth and orientation (Fig. 9). The Protected Middle and Protected Inside sites had significantly higher Ω_{Ar} than the other four sites (except in the pairwise test between Protected Middle and Exposed Middle), which further highlights the clustering of the Protected Middle and Protected Inside sites relative to the

other sites (Fig. 9). There were no site-to-site significant differences in surface Ω_{Ar} values, indicating greater homogeneity at 10 the surface. Not only were there significant differences in bottom water $\Omega_{\Lambda_{\Psi}}$ but the bottom waters were spatially decoupled as well. Throughout the year, bottom, Ω_{Ar} measurements from Protected Inside and Protected Middle were far less correlated with measurements from the deeper and exposed sites, as compared to the correlations among the deeper, more exposed sites (Fig. 10). In contrast, the surface Ω_{Ar} was highly correlated between all six sites (Fig. 10). The bottom water decoupling and surface water coupling were largely maintained during periods of both strong and weak upwelling (Fig. S8).

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4. Discussion

This study demonstrates strong spatial and temporal variability in CO₂ system chemistry within a central California kelp forest using nearly 800 DIC and TA observations that ranged across six sites, multiple depths, and spanning a period of 14 months. This data set represents one of the largest multi-parameter CO₂ system data sets completed in a kelp forest_yOur 20 spatially expansive sampling captured larger pH ranges than in many of the southern California pH studies. Our calculated range in pH of 7.7-8.33 was larger than the range observed in kelp forests from single pH sensors in the Channel Islands (Kapsenberg and Hofmann, 2016; 7.88-8.12), the La Jolla kelp forest (Takeshita et al., 2015; ~7.78-8.12), and the Santa Barbara Channel (Hofmann et al., 2011; ~7.7-8.25). Our pH range was slightly smaller than the range of ~7.65-8.39 observed by Frieder et al (2012) in the La Jolla kelp forest using a network of pH sensors, although the high temporal 25 resolution of the sensors captured event-scale variability that would likely be missed by the weekly sampling alone in our

study. We now consider the physical and biological drivers of <u>our</u> observed variability and the implications of <u>our</u> work for understanding kelp forests in an era of global change.

4.1 Mechanisms of observed variability

Co-variation of water column structure and kelp canopy biomass provided evidence for the strong influence of regional scale upwelling processes on the seasonal cycle of the kelp canopy (Fig. 2a). Bottom water advection during 30

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detecting biogeochemical change in this system

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upwelling season introduces nutrients into the kelp forest, resulting in increased kelp growth and canopy biomass (Jackson, 1977). Unlike in southern California, where upwelling and canopy biomass are not tightly coupled, central California features very strong coupling between upwelling and kelp growth (Bell et al., 2015b). This strong co-variation provides support for asserting the role of both physical and biological drivers of kelp forest biogeochemistry.

- 5 During periods of strong upwelling, water column stratification increased (Fig. 2b) due to intrusion of cold, high DIC bottom water (Figs. 3 and 8) into the deeper sites. Once bottom water was introduced to the deeper sites, it was more easily exchanged with kelp forest bottom waters on the exposed side than on the protected side. Bottom water velocities from July to December 2013, when data were available within the kelp forest on both the protected and exposed side side frager velocity variability on the exposed side than on the protected side (Fig. 11). The exposed side featured
- 10 stronger downcoast (negative alongshore) and onshore (negative cross shore) flow than did the protected side, which increased the exchange between offshore waters and the exposed side more so than on the protected side, Further physical oceanographic studies should ascertain the mechanisms responsible for the enhanced bottom water exchange on the exposed side relative to the protected side. We also recognize that higher frequency water sampling may have captured the biogeochemical signature of occasional bottom water advection into the shallower sites that was missed through weekly 15 sampling alone.

In light of all the evidence for the role of physical processes in shaping the biogeochemistry of the kelp forest, we emphasize that photosynthesis still played an important role in shaping the carbon system variability in the surface waters. Surface water pCO_2 remained undersaturated with respect to the atmosphere starting at the beginning of upwelling season and persisted throughout the summer months (Fig. 5). The persistent undersaturation of surface waters is strong evidence of

- 20 photosynthesis' role in contributing to biogeochemical variability in spring and summer months, particularly in the surface waters where the bulk of kelp biomass resides. We note that photosynthesis was likely occurring throughout most of the water column due to understory algae, but the vertical resolution of our sampling (1 mab and 1 mbs) prohibits us from being able to quantify this contribution. More vertically resolved measurements are needed to understand the role of understory. production in the kelp forest.
- 25 _____Although we are unable to quantitatively partition the photosynthetic activity between kelp and phytoplankton in the kelp forest, we note that surface pCO₂ was undersaturated as early as February 2014 (Fig. 5b), when kelp canopy biomass was near minimum values (Fig. 2a). We hypothesize that early season CO₂ uptake was controlled by the phytoplankton community in the absence of kelp. Once the kelp canopy was established several months later, the kelp played an important biogeochemical role both through direct photosynthetic uptake, as well as reducing water velocity within the
- 30 kelp forest (Rosman et al., 2007), which allowed greater biogeochemical modification of surface water chemistry through phytoplankton and kelp metabolism. This hypothesis is testable using offshore sampling sites outside the influence of the kelp forest to better quantify the phytoplankton and kelp community contributions to the observed biogeochemical variability. However, our offshore sites were only tens of meters outside of the kelp. Therefore, it is not surprising that we are unable to distinguish surface waters from within the kelp forest from those just outside the kelp. Future sampling efforts

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would benefit from utilizing offshore sites further from the influence of the kelp, as well as to utilize phytoplankton-specific tracers, such as silica (Jackson, 1977), in order to better partition the biogeochemical contributions from various functional groups within the kelp forest community.

In contrast to the evidence for surface photosynthesis, we do not see biogeochemical evidence for significant calcification within the kelp forest. Benthic calcification would have depleted TA in the bottom waters relative to the surface, yet we see no consistent pattern in the vertical TA gradients (Fig. 6b). The lack of TA gradients suggests that the biogeochemical signature of calcification in the bottom waters of the kelp forest was small relative to bottom water exchange in the kelp forest.

4.2 Implications for understanding kelp forest ecosystems in an era of global change

- 10 Our data provide critical biogeochemical baselines to assess kelp forest responses to local and global stressors, and <u>further</u> highlight the necessity of long-term, spatially expansive sampling for gaining insights into the patterns and controls on kelp forest biogeochemistry. Kelp forests are spatially and temporally dynamic environments generally found along upwelling margins, so any assessment of their biogeochemical variability must account for the variability in their seasonalto-interannual physical (Bograd et al., 2009; Checkley and Barth, 2009) and biological controls (Bell et al., 2015b). We have
- 15 demonstrated how variations in these physical and biological controls in a central California kelp forest create biogeochemically heterogeneous environments. This creates the opportunity to do localized "space-for-time" experiments to understand benthic organismal and community response to high CO₂ seawater. In contrast to larger space-for-time experiments (Hofmann et al., 2014), a single kelp forest may be sufficient for replicating the geochemical gradients expected between current conditions and future conditions under ocean acidification. These localized space-for-time experiments
- 20 could be conducted in small environments (hundreds of meters, not hundreds of kilometers) with near identical biological assemblages and for a fraction of the cost and effort. Combining transplant experiments with observational work could leverage the biogeochemical differences between areas of a kelp forest to yield important insights into the adaptive potential of benthic community members under the combined stresses of global change.
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Aqueous CO₂ variability typically does not occur in isolation of other biogeochemical and environmental changes. 25 Although we do not have the O₂ measurements to accompany our carbon system time series, co-variation of CO₂ and O₂ has been well documented in California's coastal ecosystems (Booth et al., 2012; Frieder et al., 2012; Takeshita et al., 2015) and frequent episodic hypoxia has been documented near our study site (Booth et al., 2012). While a large component of this variation is naturally occurring along upwelling margins, low O₂/high CO₂ events are predicted to increase in frequency in the future due to oxygen minimum zone expansion (Bograd et al., 2008; Booth et al., 2014; Stramma et al., 2010) and

30 increases in upwelling favorable winds (Bakun, 1990; Sydeman et al., 2014). Understanding the co-variation, or lack thereof, between critical environmental parameters (e.g., temperature, CO₂ system variables, and O₂) through long-term spatially expansive measurements is necessary to define the range and timescales of environmental conditions experienced by kelp forest inhabitants. Quantifying these environmental conditions can inform the design of more realistic laboratory

experiments, featuring proper ranges and timescales of biogeochemical and thermal variability as opposed to chemostatic conditions (Reum et al., 2015). More realistic experimental conditions will yield additional insights into organismal and community response to climate change and OA.

Our data demonstrate that, despite the strong influence of physical processes, primary production can alter local

- 5 biogeochemistry. Understanding the role of foundation species, such as giant kelp, in creating biogeochemical refugia both through metabolic activity and alteration of the hydrodynamic regime within the kelp forest via increased residence time (Rosman et al., 2007) warrants further attention in an <u>acidifying</u> ocean, as they present potential to mitigate some stress effects of low O₂, high CO₂ water. The combination of physical and biological processes may create natural refugia for certain sensitive organisms or, conversely, create particularly stressful conditions for others. Organisms that can confine
- 10 themselves to the upper water column may be able to use the locally created biogeochemical refuge to avoid <u>low pH</u>, whereas organisms that must use the entire water column will experience large ranges in carbonate chemistry (pH, pCO₂, and Ω_{Ar}) that will only grow larger with continued acidification.

In order to effectively manage critical coastal ecosystems in the face of climate change and OA, resource managers require both monitoring data and a process-based understanding of biogeochemical variability in order to identify changing

- 15 environmental conditions and forecast ecosystem responses in kelp forests (Boehm et al., 2015). Such understanding is currently lacking. Along the US west coast, states currently use decades-old water quality criteria for assessing pH, including that the pH should not drop below 6.5 and/or that it should not deviate more than 0.2 units from natural conditions (Weisberg et al., 2016). Yet we have demonstrated changes up to 0.5 pH units within a single kelp forest in just 15 meters depth. Additional observational studies may prove useful in helping us refine our understanding of coastal water quality away from
- static indicators and towards a more dynamic understanding of the ranges and controls on coastal water quality in order to better differentiate natural and anthropogenic effects, as has been demonstrated for dissolved oxygen (Booth et al., 2014).
 We recommend that <u>regulatory</u> agencies revise existing regulations to incorporate this understanding of natural variability in carbonate chemistry into their regulatory frameworks, as well as to expand the suite of carbonate chemistry water quality variables beyond pH alone (Weisberg et al., 2016). Developing stronger biological criteria for carbonate chemistry ranges
- 25 and variability deemed necessary to preserve critical marine living resources would help align scientific and management priorities by focusing research efforts on quantifying these acceptable ranges of conditions (Chan et al., 2016; Weisberg et al., 2016).

Comprehensive, spatially expansive monitoring is fundamental to characterizing the ranges and timescales of carbonate system variability in highly productive coastal ecosystems, such as kelp forests. Maintaining monitoring networks along coastal ecosystems is a crucial step to developing an understanding of natural vs. anthropogenic influences in the coastal zone in support management and regulatory efforts (Strong et al., 2014). Recent advances in sensor technology, such as the SeapHOx (Bresnahan et al., 2014), may make monitoring far less laborious than the data collection efforts in this study. However, we strongly recommend that monitoring programs measure at least two carbonate system parameters (TA, DIC, pH, pCO₂) so as to fully constrain the carbonate system (McLaughlin et al., 2015), with a goal of measuring three or

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2015) or newly developed autonomous TA sensors (Spaulding et al., 2014) may accomplish this task. Integrating observations from individual sites along the California coast into larger coordinated networks, such as the California-Current Acidification Network, will provide a more complete perspective on the spatial and temporal variability of the aqueous CO_2

system and its controls (Chan et al., 2016; McLaughlin et al., 2015).

Long-term observational data sets are also crucial for improving our process-based understanding of coastal ocean biogeochemistry. Data from studies such as these can be used to parameterize the process-based hydrodynamic-biogeochemical models that are needed to predict coastal ecosystem responses to climate change and <u>ocean acidification</u> (Boehm et al., 2015; McLaughlin et al., 2015). These models can help identify climate change and/or <u>ocean acidification</u>

- 10 hotspots along coastal ecosystems in the future and help marine living resource managers with scenario planning so that they can direct resources accordingly (Strong et al., 2014). Similarly, marine resource managers must consider the biogeochemical implications of any management activities, such as kelp harvesting, which alter kelp canopy density. We have shown considerable CO₂ uptake at our study site during periods of high kelp canopy cover. While we were not able to directly attribute the CO₂ uptake to *Macrocystis pyrifera*, the direct and indirect effects of the kelp canopy are likely to increase vertical gradients in water chemistry and therefore activities that decrease canopy density are likely to reduce
 - gradients in the water column.

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Kelp forest ecology has long been a focal point for marine ecologists. This study complements the long history of kelp forest community (Dayton, 1985; Graham et al., 2007) and disturbance ecology (Edwards, 2004; Edwards and Estes, 2006) by highlighting the dynamic biogeochemistry of kelp forests over an annual cycle. The few existing biogeochemical

- 20 studies of *Macrocystis pyrifera*-dominated kelp forest along the California coast have thus far occurred in southern California (Frieder et al., 2012; Kapsenberg and Hofmann, 2016; Takeshita et al., 2015). This study expands on the southern California studies by adding the first fully resolving CO₂ system chemistry study in a central California kelp forest where seasonality is relatively stronger and kelp cover is more variable (Bell et al., 2015b; Checkley and Barth, 2009; Reed et al., 2011).
- 25 We hope that the large data set presented here motivates the inclusion of biogeochemistry as a new approach to understand kelp forest ecosystem function and the feedbacks between biology, chemistry, and physics in these dynamic systems. We note that this study would not have been possible without a large and concerted field effort to establish a spatially expansive sampling program that ranged over gradients in kelp density and wave exposure. Yet this sampling program was necessary to generate insights into the relevant scales of kelp forest biogeochemical variability presented in this
- 30 study, variability that could not be discerned from a single sampling point or sensor alone. We advocate for monitoring efforts to extend beyond single site measurements within a kelp forest. Doing so will enhance our understanding of the biological and physical mechanisms giving rise to the observed biogeochemical variability; information crucial to accurately predicting the response of kelp forest ecosystems to global change.

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Supplement and Data Availability

Supporting figures and tables can be found in the supplement to this study. Data presented in this study are also available in the supplement.

Conflict of Interest

5 The authors declare no conflict of interest

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| Site | Latitude (°N) | Longitude | Depth (m) | Distance from |
|-----------------------|---------------|-------------|-----------|---------------|
| | | (°W) | | shore (m) |
| Protected Offshore | 36.621983 | 121.900883 | 16 | 250 |
| Protected Middle | 36.6216 | 121.90176 | 9 | 160 |
| Protected Inside | 36.62132 | 121.90195 | 7.5 | 130 |
| KFA | 36.62363 | 121.90473 | 14 | 270 |
| Exposed Offshore | 36.62316 | 121.90503 | 13.5 | 200 |
| Exposed Middle | 36.62093889 | 121.9003806 | 11 | 160 |

 Table 1: Study site characteristics. Distance from shore measured from the closest perpendicular location.

| Variable | Top/Bottom | Minimum | Mean | Maximum |
|------------------------------|------------|---------|------|---------|
| DIC (µmol kg ⁻¹) | Тор | 1853 | 2023 | 2110 |
| | Bottom | 1958 | 2093 | 2225 |
| TA (μmol kg ⁻¹) | Тор | 2213 | 2243 | 2277 |
| | Bottom | 2199 | 2249 | 2337 |
| рН | Тор | 7.92 | 8.08 | 8.33 |
| | Bottom | 7.70 | 7.96 | 8.21 |
| pCO ₂ (µatm) | Тор | 172 | 364 | 543 |
| | Bottom | 249 | 508 | 952 |
| $\Omega_{ m Ar}$ | Тор | 1.63 | 2.43 | 3.91 |
| | Bottom | 0.94 | 1.82 | 3.23 |

Table 2: Carbon system variables summary statistics aggregating all six sampling sites



Figure 1: Study site: kelp forest offshore of Hopkins Marine Station. Green shows historical average kelp canopy extent. Site names are as follows: Protected Offshore (Pro Off; black), Protected Middle (Pro Mid; red), Protected Inside (Pro Inn; magenta), Kelp Forest Array (KFA; yellow), Exposed Offshore (Exp Off; blue), and Exposed Middle (Exp Mid; cyan). Inset shows Monterey Bay with color dots corresponding to the data buoys shown in Fig. S1.







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Figure 3: Depth-resolved temperature profiles along the protected transect throughout the 14-month time series. White spaces, including October 2013 and August 2014, are missing data due to the CTD not recording or poor data removed during quality control.



Figure 4: Time series of a) DIC and b) TA. Solid lines are bottom samples and dashed lines are surface samples.



Figure 5: Time series of a) pH, b) pCO₂, and c) Ω_{Ar} calculated from TA and DIC measurements. Solid lines are bottom samples and dashed lines are surface samples.



Figure 6: Variability throughout the sampling period for a) DIC and b) TA. The range of surface values across all six sites is shown in red and the range of bottom values across all six sites is shown in yellow. The blue line is the median surface-to-bottom
 difference in DIC or TA during a given sampling day and the blue shaded region represents the maximum and minimum vertical gradients observed on each day. Note the differences in scale between a) and b).



Figure 7: Observed (black) surface-to-bottom differences in a) pH, b) pCO₂, and c) Ω_{Ar} at the Protected Offshore site along with the calculated contributions of temperature (red), salinity (magenta), DIC (blue), and TA (yellow) to the observed carbon system gradients. The residual difference between the observed and calculated contributions is shown in cyan.



Figure 8: a) Bottom DIC-bottom temperature relationships for all six sites and b) bottom-to-surface DIC gradients as a function of bottom DIC concentrations.















