PRIMARY RESEARCH ARTICLE

Coast-wide evidence of low pH amelioration by seagrass ecosystems

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Abstract

Global-scale ocean acidification has spurred interest in the capacity of seagrass ecosystems to increase seawater pH within crucial shoreline habitats through photosynthetic activity. However, the dynamic variability of the coastal carbonate system has impeded generalization into whether seagrass aerobic metabolism ameliorates low pH on physiologically and ecologically relevant timescales. Here we present results of the most extensive study to date of pH modulation by seagrasses, spanning seven meadows (*Zostera marina*) and 1000 km of U.S. west coast over 6 years. Amelioration by seagrass ecosystems compared to non-vegetated areas occurred 65% of the time (mean increase 0.07 ± 0.008 SE). Events of continuous elevation in pH within seagrass ecosystems, indicating amelioration of low pH, were longer and of greater magnitude than opposing cases of reduced pH or exacerbation. Sustained elevations in pH of >0.1, comparable to a 30% decrease in [H$^+$], were not restricted only to daylight hours but instead persisted for up to 21 days. Maximal pH elevations occurred in spring and summer during the seagrass growth season, with a tendency for stronger effects in higher latitude meadows. These results indicate that seagrass meadows can locally alleviate low pH conditions for extended periods of time with important implications for the conservation and management of coastal ecosystems.

KEYWORDS
buffer, carbon cycling, carbonate chemistry, mitigation, ocean acidification, photosynthesis, submerged aquatic vegetation, *Zostera marina*

1 | INTRODUCTION

The oceanic uptake of anthropogenic carbon dioxide (CO_2) is driving ocean acidification (OA) with a myriad of implications and threats for marine life (Kroeker et al., 2013; Orr et al., 2005). In particular, surface ocean pH has decreased globally by 0.1 pH units since the Industrial Revolution and is expected to decline an additional 0.3–0.4 pH units by the end of the century (Caldeira & Wickett, 2003).

Furthermore, some geographic regions, such as those that experience coastal upwelling, are acidifying faster than others, highlighting the urgent need to explore mitigation strategies (Feely et al., 2008; Gruber et al., 2012; Osborne et al., 2020).

Photosynthesis in marine environments is a fundamental metabolic process that influences seawater pH, and the accompanying carbonate system more broadly, and can offset OA effects through uptake of CO_2 and other forms of dissolved inorganic carbon (DIC)

(Hendriks et al., 2014; Wahl et al., 2018). Elevation in pH occurs when photosynthesis dominates over respiration (Krause-Jensen et al., 2016); this criterion applies to communities of habitat-forming marine macrophytes (e.g., seagrasses and kelps) that inhabit coastal areas worldwide (Duarte & Cebrián, 1996). As a result, these eco-systems have been proposed as potential management tools to ameliorate low pH in coastal areas (Nielsen et al., 2018). Coastal areas, however, are typically characterized by large variability in en-vironmental conditions driven by complex interactions among phys-ical and biological processes (Waldbusser & Salisbury, 2014). These processes alter the coastal seawater carbonate system and induce appreciable fluctuations in pH. Such fluctuations eclipse the smaller variability of the open ocean and can dwarf the predicted decrease in average pH due to anthropogenic CO_2 (Duarte et al., 2013; Hofmann et al., 2011; Kapsenberg & Cyronak, 2019). In particular, the metabolism of marine macrophytes often creates marked daily and seasonal fluctuations in pH (Camp et al., 2016; Hendriks et al., 2014; Krause-Jensen et al., 2016; Manzello et al., 2012; Saderne et al., 2019; Silbiger & Sorte, 2018). As a consequence of this vari-ability, the role of marine macrophytes in ameliorating exposure to low pH, in terms of timing, magnitude, extent, and relevance for organisms remains uncertain. For example, of the available studies in seagrass ecosystems, some suggest net amelioration of low pH (Buapet et al., 2013; Cyronak et al., 2018; Hendriks et al., 2014; Scanes et al., 2020; Su et al., 2020; Unsworth et al., 2012), while others suggest seagrasses may also amplify negative effects (Pacella et al., 2018). The limited spatial and temporal scales of prior studies further hinders understanding (Buapet et al., 2013; Cyronak et al., 2018; Hendriks et al., 2014; Pacella et al., 2018; Saderne et al., 2013, 2019; Semesi et al., 2009; Unsworth et al., 2012).

Here we present results of a study encompassing ~1000 km of coastline along the U.S. west coast that incorporates 6 years of data collected from seven seagrass meadows of *Zostera marina*, the most widespread seagrass species in the northern hemisphere (Green & Short, 2003). We deployed autonomous sensor packages in seagrass meadows to continuously record the seawater carbon-ate system for comparison to that of adjacent, non-vegetated con-trol areas. The sensors quantified in situ pH (total scale), dissolved oxygen, temperature, salinity, instantaneous water depth, and flow speed. We also collected data on seagrass morphological and eco-system traits during each sensor deployment. We then defined "low pH amelioration" as the case when pH within a seagrass meadow exceeded that outside (i.e., positive ΔpH), and "low pH exacerba-tion" when ΔpH was negative. We explored relationships between ΔpH and potential biological, environmental, and hydrodynamic drivers to ascertain the primary controls on the seawater carbon-ate system in seagrass ecosystems. Our results demonstrate that, despite strong spatiotemporal variability, seagrass ecosystems can sustain prolonged periods of elevated seawater pH. This finding un-derscores that amelioration of low pH should join the list of other recognized ecosystem services provided by seagrasses, reinforcing the importance of protecting and restoring these habitats.

2 | MATERIALS AND METHODS

2.1 | Experimental design

The study was performed at seven sites with *Z. marina* sea-grass meadows spanning ~1000 km along the coast of California (Figure 1). The California coast includes two important oceano-graphic regions. Northern California, dominated by the California Current, is an upwelling region with cooler and more CO_2-rich waters brought up near the surface seasonally, while Southern

FIGURE 1 Differences in pH between seagrass ecosystems and non-vegetated areas. (a) Histogram of pH within the seagrass ecosystems (green) and nearby non-vegetated areas (brown) pooled across all deployments, where the dashed lines show mean values. (b) Histogram of the level of amelioration or exacerbation of low pH in seagrass ecosystems (ΔpH), pooled across all deployments, where the dashed line shows the mean value. (c) Spatial extent and locations of the seagrass meadows examined in California, USA; Site abbreviation: BH, Bodega Harbor; CP, Cypress Point; CR, Chicken Ranch; EK, Elkhorn Slough; MB, Mission Bay; NP, Newport Bay; TP, Tom's Point. The magnified inset depicts Tomales Bay

California, dominated by the Southern California Countercurrent, is a region with less intense upwelling and where waters are warmer and less CO_2 rich (Feely et al., 2016; Newman, 1979). The sites were selected along the different regions because of their similar estuarine geomorphological conditions (tidal estuaries), non-carbonated muddy silicate sediments (less than ~7% of $CaCO_3$), and the presence of *Z. marina* continuous seagrass meadows (larger than 0.5 km²) and non-vegetated mud flats at similar depths (see Table S1 for more details).

At each site, we deployed autonomous recording sensor packages inside seagrass ecosystems and outside, in non-vegetated control areas at similar depths (1–2 m depth at the lowest tide) situated ~500 m away from the seagrass meadow edge. As all sites are tidally dominated characterized with bidirectional flow, sensors were set up parallel to the main dominant current. Sensors collected continuous data of pH, dissolved oxygen, temperature, salinity, water pressure, and current flow every 10 min.

Deployments were made from 2014 until 2019 spanning all four seasons (see Table S1). A total of 29 independent deployments were completed, each with a duration between 1.5 and 4 weeks. Between deployments, sensors were held at the laboratory in filtered seawater. A week before each deployment, sensors were activated, conditioned in flowing seawater in tanks at laboratory facilities, and checked for proper functioning prior to installation in the field (Bresnahan et al., 2014; Rivest et al., 2016).

The sensor packages were composed of a SeapHox (pH, temperature, salinity, dissolved oxygen, water pressure) or a SeaFET (pH, temperature) from SeaBird Scientific in combination with a MiniDot (dissolved oxygen, temperature) from Precision Measurement Engineering (PME). SeaFET and SeapHox pH sensors utilize the Honeywell Durafet combination electrode (Bresnahan et al., 2014; Martz et al., 2010; Takeshita et al., 2014). The sensor packages were attached to a metal frame and moored horizontally within the meadow's canopy or unvegetated bottom on two metal poles anchored to the sediment with the sensing electrodes (SeaFET) and pump (SeapHox) situated 20 cm above the seafloor. Nortek Acoustic Doppler Velocimeters (ADV) were deployed within 1 m of each sensor package, one within the seagrass meadow and one outside in the non-vegetated area. The ADV's sensor heads were pointing upward to capture flow measurements at the canopy height, where data were collected every 2 h for a burst duration of 10 min, with a sampling frequency of 1 Hz. Some deployments happened simultaneously within the same site but at a different location within the seagrass meadow. As a consequence, not all deployments had corresponding ADV data.

Discrete water samples for pH and total alkalinity (A_T) were collected over the duration of each deployment using a Niskin bottle immediately adjacent to the sensor during high tide. The water samples for pH were transferred to 250-ml borosilicate glass bottles and preserved with 100 µl of saturated $HgCl_2$ in cool temperatures (4°C), while the water samples for A_T were transferred to 250-ml plastic Nalgene bottles and frozen. Although alkalinity is largely conservative, freezing stops most of the biological activity assuring robust measurements

without affecting results (data not shown). All samples were returned to the Bodega Marine Laboratory – University of California, Davis, for analysis. The number of discrete water samples varied from 2 to 10 per deployment, a subset of which included duplicates or triplicates. Additionally, salinity and temperature data were recorded at the same time of bottle sampling using a calibrated Yellow Springs Instruments Professional Plus Multiparameter meter (YSI ProPlus).

Honeywell Durafet pH sensors were calibrated based on field discrete water samples following best practices (Bresnahan et al., 2014). The pH was calculated from the internal reference electrode and reported in total scale at in situ temperature and salinity conditions (Rivest et al., 2016). The mean difference between reference samples and the sensor measurements was 0.01 (±0.006 SD), which meets the Global Ocean Acidification Observing Network (GOA-ON) weather-level data quality objectives and allows the use of pH data for the purposes of this study (Newton et al., 2014). Pressure data from SeapHOx sensors were calibrated with ADV pressure data from each deployment. Factory calibrations were used for the oxygen optodes (Aandera, SeapHOx; MiniDOts, PME) and salinity, and temperature (SBE-37 MicroCAT, Seabird).

2.2 | Sample analysis

Seawater pH of the discrete water samples was determined on the total scale with one of two high-precision spectrophotometers using unpurified m-cresol purple dye (Clayton & Byrne, 1993). A Submersible Autonomous Moored Instrument pH analyzer (SAMI-pH; Lai et al., 2018; Martz et al., 2003; Seidel et al., 2008) from Sunburst modified for benchtop function was used from 2014 to 2017 (m-cresol purple dye was prepared and calibrated by the manufacturer, sensors S80 07/23/12 and S83 06/12/14); and an Ocean Optics Jaz Spectrophotometer EL200 was used from 2017 to 2019 (m-cresol purple dye from Sigma-Aldrich, MKBR3556V and Acros Organics, AO394755 since 2019). Water samples were kept in a temperature-controlled water bath (Thermo Scientific, Precision Microprocessor Controlled 280 Series) at 25°C before analysis to minimize temperature-induced errors in absorbance measurements. Each pH instrument was validated by analyzing TRIS buffer revealing that the system was accurate to within 0.005 pH units. The carbonate system software package, CO2SYS Version 2.1 for MS Excel (Pierrot & Wallace, 2006), was used to calculate in situ pH values using in situ salinity and temperature measurements. Seawater A_T was measured using open-cell titration with triplicate samples (Metrohm 855 Robotic Titrosampler, Metrohm) using 0.1 N HCl (Fisher Chemical) diluted to a nominal concentration of 0.0125 M. Acid concentration was calibrated by analyzing Certified Reference Material (CRM) from A. Dickson's laboratory before each titration session. For each set of triplicate analyses, the median value was considered. Instrumental precision from 50 of the analyses of CRM batches over the course of the study was SD <5 µmol kg⁻¹. To provide a complete description of the seawater carbonate system (Table 1; Table S1), parameters were estimated from pH and A_T, using

TABLE 1 Characteristics of the seawater carbonate system in seagrass ecosystems and non-vegetated areas

Parameter	Seagrass					Non-vegetated				
	Mean	SD	Min	Max	N	Mean	SD	Min	Max	N
pH_T	7.98	0.14	7.46	8.60	5162	7.91	0.12	7.41	8.34	5162
Total alkalinity ($\mu mol\ kg^{-1}$)	2296	73	1890	2485	131[a]	2297	72	1948	2485	132[a]
Estimated pCO_2 (μatm)	518.25	179.26	76.05	1842.74	—	607.8	202	187.59	2018.02	—
Estimated DIC ($\mu mol\ kg^{-1}$)	2109	87	1679	2368	—	2140	80	1833	2397	—
Estimated Ω_{Ar}	2.2	0.7	0.8	6.9	—	1.9	0.5	0.7	4.0	—
Temperature (°C)	15.96	3.15	8.72	24.82	5162	15.82	3.20	8.43	25.14	5162
Salinity	32.98	1.17	25.82	34.56	5162	32.97	1.15	26.87	34.58	5162
Dissolved oxygen ($\mu mol\ kg^{-1}$)	225	59	39	549	4094	229	43	71	402	4092

Note: Estimated carbonate chemistry parameters were calculated for the whole dataset based on the relationship between salinity and total alkalinity from discrete samples (see methods, section 2.2).

Abbreviations: Ω_{Ar}, aragonite saturation state; DIC, dissolved inorganic carbon; N, sample size of parameters measured in situ every 10 min, averaged per hour.

[a]Total number of discrete samples.

the *seacarb* R package (Gattuso et al., 2019) and assuming published values for constants K_1 and K_2 (Lueker et al., 2000), K_f (Perez & Fraga, 1987), and K_s (Dickson, 1990). The A_T in the time series was estimated from salinity values in sensors, based on linear regressions between salinity and A_T of the discrete water samples. Independent regressions were done for each site (Bodega Harbor [BH]: $R^2 = 0.69$, $p < 0.001$, $df = 38$; Tom's Point [TP]: $R^2 = 0.33$, $p < 0.001$, $df = 32$; Cypress Point [CP]: $R^2 = 0.76$, $p < 0.001$, $df = 22$; Chicken Ranch [CR]: $R^2 = 0.52$, $p < 0.001$, $df = 9$; Elkhorn Slough [EK]: $R^2 = 0.36$, $p < 0.001$, $df = 10$; Newport Bay [NP]: $R^2 = 0.31$, $p < 0.001$, $df = 15$; Mission Bay [MB]: $R^2 = 0.25$, $p < 0.001$, $df = 26$). Only pH values measured in situ are used for further data analysis. Uncertainties of the derived parameters (DIC, pCO_2, and Ω_{Ar}) were quantified using a Monte Carlo analysis (100 simulations; Takeshita et al., 2021) on two deployments. These two deployments were chosen to represent a high (±38 $\mu mol\ kg^{-1}$) and low (±8 $\mu mol\ kg^{-1}$) uncertainty in the A_T-salinity relationship. For each simulation, normally distributed errors were introduced into pH (± 0.01) and A_T (±25 $\mu mol\ kg^{-1}$). The overall uncertainties of the derived parameters were calculated as one standard deviation of the simulations. On average, uncertainties for pCO_2 (2.5%–3%) and Ω_{Ar} (0.02–0.05) were similar for both sites, as the calculations for these parameters are not particularly sensitive to A_T. For pCO_2, uncertainty is higher at lower pCO_2, whereas uncertainty is lower for Ω_{Ar} at lower Ω_{Ar}. The uncertainty for DIC was similar to the uncertainty in A_T, that is, ±33 and ±8.7 $\mu mol\ kg^{-1}$ for the high and low A_T uncertainty, respectively.

2.3 | Seagrass sampling

For each deployment, a 50 cm × 50 cm quadrat was deployed every 10 m in an 80 m linear transect starting at the sensor package within the seagrass meadow. In each quadrat, measures of shoot density were taken, and five seagrass shoots were collected and kept on ice during transport to the laboratory. In the laboratory, the longest leaf of each shoot was measured for maximum length and width. The seagrass leaf area index (LAI) was calculated as the average surface area of the leaf (length × width of the longest leaf) multiplied by the average seagrass shoot density (shoots m^{-2}). LAI was chosen over other parameters because this metric integrates different structural parameters, reflecting the density of photosynthetic tissues, and has already been proposed as a main control of pH in seagrass meadows (Hendriks et al., 2014).

2.4 | Statistical analysis

Data from sensors were excluded during times of sensor biofouling and/or sensor malfunctioning and obvious outliers (Bresnahan et al., 2014; Rivest et al., 2016). Prior to further analyses, two datasets were generated by averaging different time intervals, 1 h and 24 h. Then, each dataset was homogenized to achieve the same sample size per deployment. To homogenize sample size, a random selection of data was done on each sensor based on the data length of the shortest time series collected. Bootstrap iterative resampling ($n = 1000$) confirmed a negligible bias on the mean (<0.0001) and standard error (SE < 0.005) of each dataset for pH data in seagrass ecosystems and non-vegetated areas. Then, we calculated the amelioration or exacerbation of low pH (ΔpH) in seagrass meadows by subtracting pH in the non-vegetated areas from the pH in the seagrass ecosystems at each hourly or daily time point. Tables and figures show hourly averaged values unless otherwise indicated.

For each ADV record, mean velocity of the water flow ($\bar{u}$) was calculated as the vector sum of the two horizontal individual squared velocities, neglecting the much smaller vertical values, averaging across each burst and then further averaging per 24 h. Root mean square velocity (RMS water velocity) was calculated as the root mean square of the mean velocity of the water flow averaged per

24 h. This quantity serves as a measure of how much the individual velocity measurements fluctuate from the mean, and therefore provides a simple metric of overall water motion, which among other effects, acts to disperse and dilute the metabolic signature of the seagrass in seawater chemistry.

We used linear simple models (LM) to evaluate the relationship between pH and dissolved oxygen in seagrass meadows and non-vegetated areas, and also to check for differences in the duration of events of low pH amelioration above a certain ΔpH threshold. In both cases we used the complete time series. For the latter, we took the most conservative approach to calculate the duration of events, as we considered events to be distinct even when ΔpH decreased below the chosen threshold for just 10 min. We used linear mixed effects models (LMMs) to determine how pH varied as a function of the type of habitat (seagrass vs. non-vegetated), and how ΔpH varied as a function of day–night light periods, season of the year, seagrass productivity period, and sites. Day–night light periods were classified based on sunrise and sunset times per each day. Seasons of the year were classified based on the four divisions of the year in temperate areas. Seagrass productivity periods were classified based on the growth season (April through September) and senescence season (October through March) for the seagrass species *Z. marina* in California. All these models were run with the independent categorical variable of interest as the fixed effect and deployment as the random effect (fixed slope, varying intercept). To avoid biases based on the unbalanced design, for the comparison between seasons we only included the sites that presented data in most seasons; and we only included data from spring and summer for the comparison among sites, as data from these seasons were available for all sites. All the LMMs were developed with the dataset averaged by 24 h time intervals except for the day–night light period comparison where we used the dataset averaged by 1 h time intervals. Models were generated with the *lme4* R package (Bates et al., 2014). Before full models were generated, the applied random effect was determined by contrasting null models with different random structures: deployment, deployment within each site, and deployment within each season. Best random structure (i.e., deployment) was chosen by performing a likelihood ratio chi-square test to assess model significance, which tests whether reduction in the residual sum of squares is statistically significant or not. The significance of the fixed effects was evaluated by comparing each full model to the null model performing a likelihood ratio chi-square test, and also comparing Akaike's information criterion (AIC). Fixed effects were considered for AIC differences bigger than 2 and a *p* < 0.05. Normality and homoscedasticity were explored via visual estimation of trends of model residuals (errors associated with homogeneity of variance, independence, and normality). Temporal autocorrelation on model residuals was assessed by plotting autocorrelation function coefficients as a function of lag k (abscissa) in correlograms.

We used principal component analysis (PCA) to assess the relationships between environmental and biological controls and the seagrass amelioration of low pH. In particular, we examined the relationships among seagrass amelioration or exacerbation of low pH (ΔpH), daylength, pH in seagrass, temperature, pCO_2 of the surrounding water (that from non-vegetated areas), water column height, RMS water velocity, and seagrass LAI. The PCA was developed with the dataset averaged by 24 h time intervals. All data were standardized to account for differences in measurement units. For standardization, we subtracted the minimum from the value of interest, and then divided by the difference between the maximum and minimum value.

3 | RESULTS

3.1 | The seagrass seawater carbonate system and the amelioration of low pH

Seagrass ecosystems in our study exhibited higher average pH in comparison to non-vegetated areas (null vs. full LMM, χ^2 = 81.227, *df* = 1, *p* < 0.001, Table S1), with a mean pH of 7.98 ± 0.002 SE within seagrass ecosystems, and a mean pH of 7.91 ± 0.001 SE in non-vegetated areas (Figure 1a; Table 1). Extreme values of pH also differed across these environments. Maximal values of pH were achieved within seagrass ecosystems (pH = 8.60), while pH minima were similar between seagrass ecosystems and non-vegetated areas (pH ~ 7.4; Figure 1a; Table 1). Overall, the pH was higher in seagrass ecosystems for 65% of the measurements (Figure 1b).

All pH time series collected in this study exhibited high-frequency daily fluctuations (Figure S1). The amplitude of pH daily fluctuations, or maximum change of pH over a 24-h cycle, was as high as 0.97 pH units, with an average amplitude of 0.29 ± 0.007 SE, for seagrass and up to 0.92 pH units, with an average amplitude of 0.23 ± 0.005 SE, for non-vegetated areas. Four dominant patterns capture the characteristics of when and how low pH amelioration or exacerbation arises (Figure 2; Figure S1). From the most common pattern to the least common, we observed: (1) a positive offset where pH is uniformly higher in seagrass ecosystems (Figure 2a); (2) similar pH minima in both seagrass and non-vegetated areas with excursions to relatively higher pH values during the day in seagrass ecosystems (Figure 2b); (3) a negative offset (Figure 2c); (4) similar baseline with a higher pH in seagrass during the day but lower pH during the night compared with non-vegetated areas that have less variability (Figure 2d). The relationship between pH and dissolved oxygen concentration illustrates the coupling between primary productivity and carbonate chemistry, and thus indicates that the metabolic activities of photosynthesis and respiration largely control pH in seagrass ecosystems and in non-vegetated areas (linear regression, for seagrass: R^2 = 0.43, *df* = 96,091, *p* < 0.001; for non-vegetated areas: R^2 = 0.39, *df* = 79,286, *p* < 0.001), although other processes likely also contribute to variation in pH. These different patterns (Figure 2) were sometimes present during the same deployment (Figure S1), suggesting that drivers such as hydrodynamic or environmental factors may modulate the metabolic pH signal (Cyronak et al., 2018, 2020; Hendriks et al., 2014; Hurd, 2015; James et al., 2020; Koweek et al., 2018). In addition, trends in the pH time series (i.e., an increase or decrease in mean pH over several days), if found, were coincident

in seagrass and non-vegetated areas, and were related to tidal cycles (Figure S1).

Generally, peaks in pH occurred during periods of high solar input (Figure 3). Hourly averaged pH values in a daily composite across
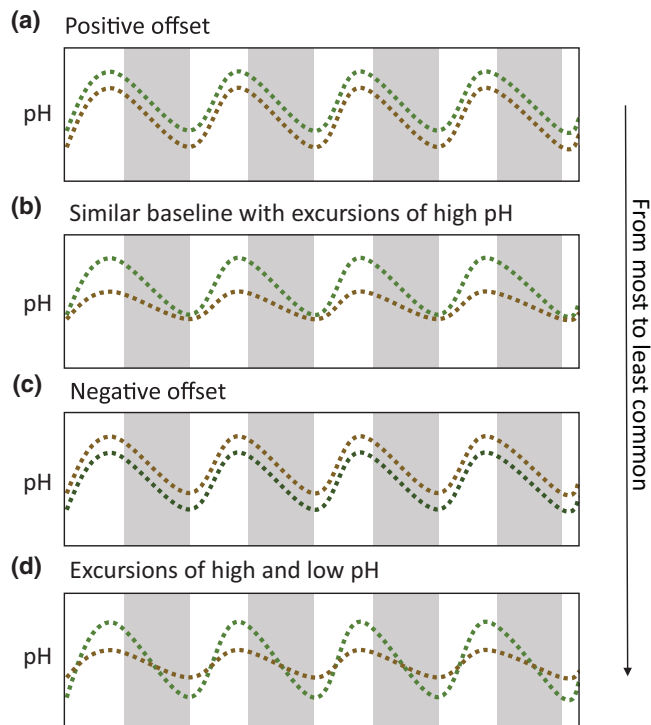
(a) Positive offset

pH

(b) Similar baseline with excursions of high pH

pH

(c) Negative offset

pH

(d) Excursions of high and low pH

pH

From most to least common

FIGURE 2 Diagram of four representative pH patterns observed in this study. Each letter on the figure, (a), (b), (c), and (d), represents a pattern arising from the comparison of pH time series in seagrass ecosystems (green) and non-vegetated areas (brown). Patterns are ordered from the most to the least observed pattern. Shaded bars represent nighttime. See text for a detailed description of each pattern

all deployments were consistently higher in seagrass ecosystems compared to non-vegetated areas, where seagrass ecosystems also presented larger maximal values of pH and variability (greater range) during the daytime hours (Figure 3a). This finding is in accordance with the most common patterns found in the time series, which included both an upward shift in pH overall (Figure 2a), and a disproportionate rise in daytime pH compared to a muted decrease in pH during nighttime (Figure 2b). Distinct monthly and seasonal patterns in pH were also observed, where pH across all deployments tended to be higher but also more variable within seagrass ecosystems (greater range) throughout spring and summer months (Figure 3b).

Despite the daily fluctuations in pH, seagrass ecosystems elevated pH above that of non-vegetated areas for extended durations of time (Figure 4). This trend can be ascertained by tracking the amount of time over which the ΔpH for a given seagrass meadow (computed relative to its adjacent non-vegetated control area) continuously exceeded a specified threshold. Events of continuous elevation in pH within seagrass ecosystems compared to non-vegetated areas (positive ΔpH, indicating low pH amelioration) were longer and of greater magnitude than opposing cases of reduced pH (negative ΔpH, indicating low pH exacerbation) (LM, *df* = 10, *F* = 22.324, *p* < 0.001; Figure 4). The duration of amelioration events was variable as a consequence of the high-frequency pH fluctuations (e.g., durations from 0.16 to 500 h for an amelioration threshold of 0.1 pH units). However, in many cases amelioration events substantially exceeded the duration of a single day–night light cycle (24 h).

3.2 | Temporal and spatial variability of the amelioration of low pH in seagrass ecosystems

Amelioration of low pH occurred in both daytime and nighttime, where the differences in ΔpH between daytime and nighttime were
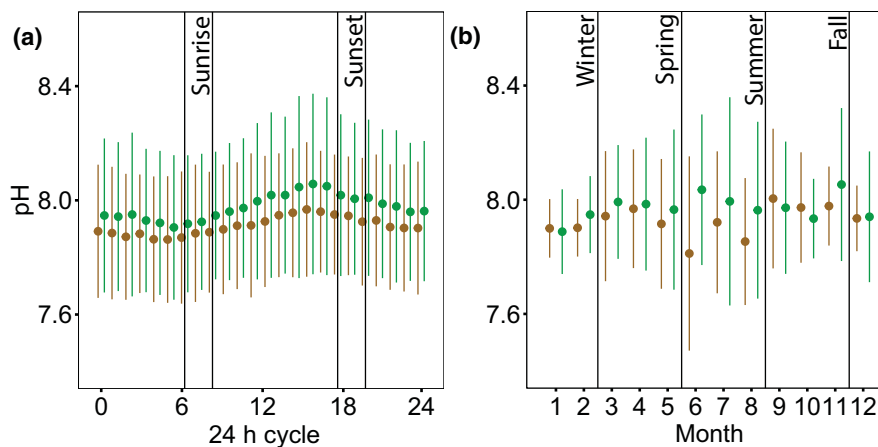
FIGURE 3 Fluctuations of pH across daily and monthly scales. Temporal variation within seagrass ecosystems (green) and non-vegetated areas (brown) across all deployments. Dots represent the mean and the vertical lines indicate ±SD. (a) Daily variation of pH shown per hour of the day, where pH was consistently higher in seagrass ecosystems compared to non-vegetated areas and also presented larger variability during the daytime hours. (b) Seasonal variation shown per month of the year, where pH tended to be higher and more variable within seagrass ecosystems throughout spring and summer months
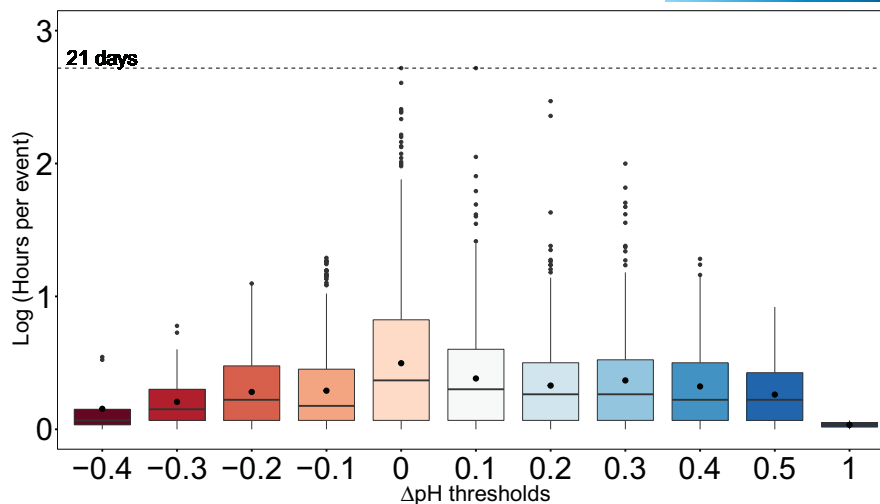
FIGURE 4 Duration of events of continuous amelioration or exacerbation of low pH as a function of the magnitude of pH change induced in seagrass ecosystems. Boxplots of ΔpH thresholds where seagrass amelioration of low pH corresponds to cases of positive ΔpH (higher pH in seagrass ecosystems, cool colors) while exacerbation of low pH corresponds to negative ΔpH (higher pH in non-vegetated areas, warm colors). Each data point represents one single event of continuous ΔpH above or below a certain threshold during a given time series, where pH was measured every 10 min. Data on the Y-axis is log-transformed (base 10) to facilitate visualization. Overall, positive amelioration events were of longer duration and of greater magnitude, with pH elevations of >0.1 unit lasting for up to 21 days. Boxplots represent median and quartiles (0.25, 0.75), whiskers represent scores inside the 1.5*Interquartile range (IQR). Mean values are shown with a black dot within the box
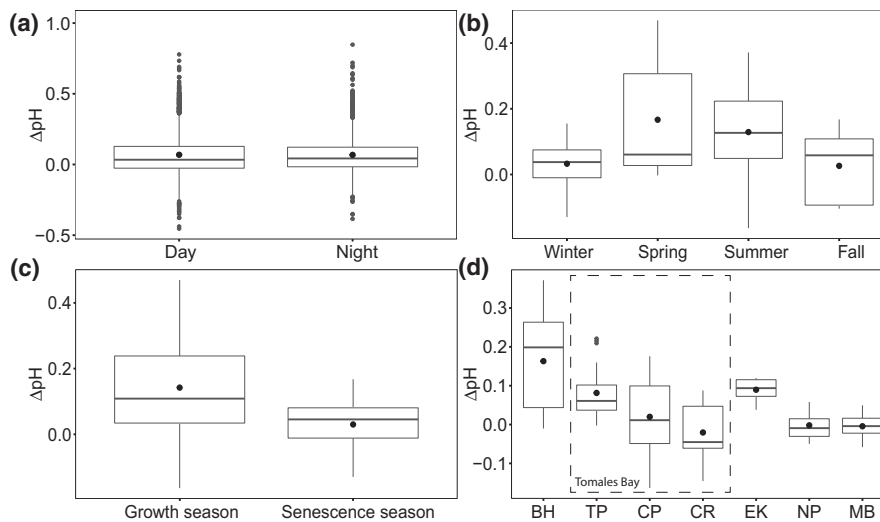

FIGURE 5 Temporal and spatial variability of the amelioration or exacerbation of low pH in seagrass ecosystems. (a) ΔpH during daytime compared to ΔpH during nighttime (n_{day} =2267 h, n_{night} =2083 h, n = 150 h/deployment; n = 29 deployments); (b) comparison of ΔpH among seasons, only including sites sampled in most seasons (BH, TP, CP), (n_{winter} =34 days, n_{spring} =32 days, n_{summer} =64 days, n_{fall} =22 days; n = 8 days/deployment; n = 19 deployments); (c) comparison of ΔpH between seagrass productivity periods, only including sites sampled in most seasons (BH, TP, CP), (n_{growth} =96 days, $n_{senescence}$ =56 days; n = 8 days/deployment; n = 19 deployments); (d) comparison of ΔpH among sites, only including spring and summer seasons (n_{BH} =48 days, n_{TP} =24 days, n_{CP} =24 days, n_{CR} =8 days, n_{EK} =8 days, n_{NP} =24 days, n_{MB} =16 days; n = 8 days/deployment; n = 19 deployments). Sites in panel (d) are ordered from north to south, from left to right, including three seagrass meadows within Tomales Bay. See Figure 1 for full site names. Data points in (a) represent hourly averages from each deployment. Data points in (b), (c), and (d) represent daily averages from each deployment. Boxplots represent median and quartiles (0.25, 0.75), whiskers represent scores inside the 1.5*Interquartile range (IQR). Mean values are shown with a black dot within the box

trivial but marginally higher at night (null vs. full LMM, χ^2 = 15.997, df = 1, p < 0.001; Figure 5a; Table S2). This finding confirms that, in most cases, the increase in pH inside seagrass beds relative to the non-vegetated areas observed during the day is maintained throughout the night (e.g., Figure 2a), such that even during the nighttime, seagrass meadows can still be influenced by preceding daytime buffering. Differences in ΔpH were significant among seasons (null vs. full LMM$_{four seasons}$, χ^2 = 14.405, df = 3, p = 0.002; null vs.

full LMM$_{growth vs. senescence}$, χ^2 = 14.34, df = 1, p < 0.001). The extent of low pH amelioration was higher in spring and summer and declined in fall and winter (Figure 5b; Table S2), with higher amelioration coincident with the active growth season of the plants (Figure 5c; Table S2). Differences in ΔpH were also apparent among sites (null vs. full LMM, χ^2 = 14.798, df = 6, p = 0.022), with a trend toward amelioration in northern sites and no amelioration or even exacerbation in southern sites (Figure 5d; Table S2).

3.3 | Controls on seagrass amelioration of low pH

The synchronicity of biological and environmental factors that increase seawater pH (e.g., photosynthesis, temperature, irradiance) with favorable seawater hydrodynamics (e.g., slack low tides with limited water movement) likely drive patterns of amelioration of low pH (ΔpH) in seagrass ecosystems (Koweek et al., 2018). Using a PCA, we assessed the relationships between ΔpH and multiple potential drivers (Figure 6). A PCA is often used to reduce the dimensionality of large datasets, by transforming a large set of variables that are usually correlated into a set of orthogonal "principal components" that specify the main axes of total variation across all parameters. The first and second principal components are of special interest because they explain the highest proportion of the total variance. Here, the first principal component explained 35.7% of the total variance and captured strong seasonal differences (see points that are
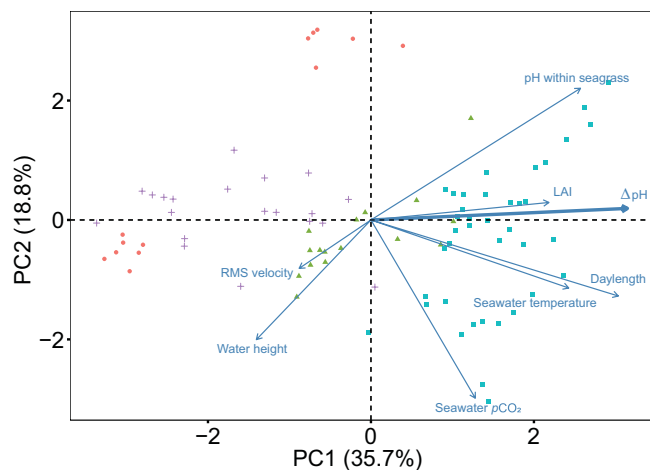

FIGURE 6 Principal component analysis of the controls of the amelioration of low pH in seagrass ecosystems. Biplot of variable vectors showing the correlation between the variables, the principal components, and individual factors. The direction of the arrows is determined by the eigenvectors that relate each variable to the two primary principal components. The direction of the arrows indicates that the values of that variable increase in that direction. Data points represent daily averages from each deployment. Colors represent the different seasons measured: blue squares = summer; green triangles = spring; red circles = fall; purple crosses = winter. Abbreviations for the individual factors are as follows: LAI = leaf area index; RMS velocity = root mean square water velocity; seawater pCO_2 = partial pressure of CO_2 in the non-vegetated areas

from summer on the right, and winter and fall on the left of Figure 6). We also see the ΔpH vector aligned closely with the first principal component, indicating a positive correlation (r = 0.49). Likewise, positive correlations were found between the first principal component and temperature (r = 0.38), daylength (r = 0.48), LAI (r = 0.34), and pH within seagrass (r = 0.40). All of these factors would be expected to positively influence the capacity of seagrass meadows to uptake DIC through photosynthesis (Fourqurean et al., 1997; García-Reyes & Largier, 2012; Hendriks et al., 2014). In contrast, negative correlations were apparent between the first principal component and water height (r = −0.22) and the RMS of water velocity (r = −0.14). RMS velocity provides a rough metric of overall water motion within a seagrass meadow, and thus, the strength of dispersion processes that reduce water residence time. The factors of water height and RMS velocity therefore characterize together two fluid dynamic properties that tend to decrease the seagrass capacity to alter seawater chemistry by diluting and dispersing the signature of plant metabolic processes. Thus, greater water depth and water flushing rates would be expected to decrease the magnitude of ΔpH. The second principal component explained 18.8% of the total variance and was negatively correlated with the pCO_2 of the surrounding water (r = −0.64), temperature (r = −0.24), water height (r = −0.43) and positively correlated with pH within seagrass (r = 0.47). Many of these latter factors can vary geographically and over shorter time periods than season, and the second principal component may capture aspects of this higher frequency variability, especially during the summer season (see high dispersion of blue points).

4 | DISCUSSION

4.1 | Potential for seagrass ecosystems to ameliorate low pH in coastal areas and management implications

Our study is the most extensive in situ high-frequency assessment of pH in seagrass meadows to date. It confirms, through empirical evidence collected across broad oceanographic and biogeographic regions (Feely et al., 2016; Newman, 1979), that pH tends to be higher within seagrass ecosystems compared with adjacent non-vegetated areas. Important seasonal and geographic patterns modulate this broad trend, where the magnitude and duration of pH amelioration events within seagrass meadows are larger than those of pH exacerbation events. Consistent with prior studies (Frankignoulle & Distèche, 1984; Hendriks et al., 2014), the highest amelioration of low pH is observed during spring and summer, coincident with the peak of productivity and growth of temperate seagrasses. This finding, together with the coupling found between pH and DO, indicates that aerobic metabolism dominates the reported patterns. However, other processes might be involved, as the correlation between pH and DO presented some anomalies (i.e., low R^2). The shorter air–sea exchange timescale for oxygen compared to CO_2, or a decoupling between decomposition and primary production driven by mixing

of water masses, might also contribute to these results but requires further exploration (Lowe et al., 2019).

Our results also suggest the existence of geographic variation in the amelioration of low pH by seagrass ecosystems that may be related to different, potentially interactive processes. During spring and early summer, upwelling events are characteristic at our northern study sites (Feely et al., 2008; García-Reyes & Largier, 2012) and may increase seagrass photosynthetic rates due to the oceanographic influx of nutrients and aqueous CO_2 into the coastal zone (Invers et al., 2001; Koch et al., 2013; Zimmerman et al., 2017). The highest amelioration of low pH is found in the northern sites that are more exposed to the open ocean (see the gradient within Tomales Bay, Figure 5) and tend to experience stronger, more sustained upwelling events compared to southern sites. In addition, there is strong morphological variation in seagrass species traits between northern and southern sites (e.g., we found longer seagrass leaves in the north) that are likely to drive higher seagrass productivity and greater amelioration of low pH in the northern sites, although photosynthetic rates were not measured in our study. Seagrass physiology and the effects of biotic and abiotic environmental drivers on seagrass metabolism are well studied, but our understanding of how those factors, in combination, affect the seawater carbonate system is still limited, since many of the drivers discussed above can also affect the seawater carbonate system independent of the seagrass metabolism. Such complexity highlights the need for further studies to fully discern the importance of different controls of pH in seagrass ecosystems and direct the selection of sites where the amelioration of low pH by seagrasses could be an effective OA management strategy.

Although our study characterizes the effect of seagrass on the seawater carbonate system, it remains unclear how these chemical changes might influence the responses of calcifying and non-calcifying organisms associated with these ecosystems. Many species that live within or very close to seagrass meadows are considered highly vulnerable to OA (Barton et al., 2012; Groner et al., 2018; Hettinger et al., 2013; Miller et al., 2016; Thomsen et al., 2015). Some examples in the study area are the oysters *Ostrea lurida* and *Crassostrea gigas* (the latter being a non-native species mostly found in on-site aquaculture facilities) and the Dungeness crab *Cancer magister* (which is the basis of an economically important fishery along the U.S. west coast). Impacts to physiological or ecological performance in these species can occur with more modest pH reductions than the elevations in pH that we observed in seagrass meadows (Barton et al., 2012; Groner et al., 2018; Miller et al., 2016; Thomsen et al., 2015). However, sensitivity to OA is driven not only by the intensity of exposure but also its duration (Waldbusser et al., 2015; Waldbusser & Salisbury, 2014). Yet, for most organisms we do not know if thresholds in the intensity or duration of low pH events exist that would critically impact performance, as most of the research has only used two or three static mean pH values for exposure (Kroeker et al., 2010, 2013). Thus, it is still unknown whether organisms are most sensitive to changes in mean versus minimum or maximum pH, and how these sensitivities might vary among response variables (e.g., calcification, growth, survival). Moreover,

other environmental stressors (e.g., temperature, turbidity) can preclude organisms to benefit from the favorable carbonate chemistry. There are also many complex community interactions that must be considered when exploring the ability of seagrasses to ameliorate OA to a degree that will have a net positive benefit to particular species (e.g., predation risk can be higher within a seagrass meadow; Lowe et al., 2019). Additional paired chemical and biological studies should focus on addressing these gaps.

Although longer term amelioration of low pH may have greater potential benefits in general, short-term carbon drawdown on hourly to daily scales can be especially important when such events coincide with times of heightened organismal sensitivity such as during a species' early life stages (i.e., larvae; Waldbusser et al., 2013). OA refugia are most relevant to sensitive organisms particularly when exposed to undersaturated waters (Kroeker et al., 2013; Waldbusser & Salisbury, 2014). In upwelling areas, those conditions often occur in spring and summer, aligning with times when seagrass pH amelioration was also highest. Our results suggest that seagrass ecosystems could protect vulnerable organisms from extreme episodic pH conditions and provide temporary chemical refugia to improve calcification and/or limit the time spent below critical physiological thresholds in pH. Moreover, this study demonstrates how amelioration of low pH can extend over physiologically and ecologically relevant timescales (e.g., elevations of pH higher than 0.1 for up 21 days, or higher than 0.3 for up to 4 days), and counters concerns that marine macrophytes might only confer OA refugia during daytime hours (Hendriks et al., 2014; Kapsenberg & Cyronak, 2019; Middelboe & Hansen, 2007; Semesi et al., 2009).

Enhanced carbon sequestration through conservation and restoration of vegetated ecosystems is of crucial importance for future scenarios of climate change (IPCC, 2014). Seagrass ecosystems are recognized as important carbon sinks that can reduce global atmospheric CO_2 concentrations through burial of organic carbon and long-term storage within the sediments (Fourqurean et al., 2012; Kennedy et al., 2010). As a result, seagrasses are now being considered in national greenhouse gas reduction schemes (Hiraishi et al., 2013; Serrano et al., 2019; Thomas, 2014). We present evidence supporting that in addition to their global role in carbon sequestration, seagrass ecosystems could also be leveraged as local management tools to mitigate the consequences of OA. Moreover, seagrasses are understood to be currently limited by CO_2 availability (Koch et al., 2013) and an increase in CO_2 concentration in the water due to OA is expected to increase their productivity (Sand-Jensen et al., 2007; Zimmerman et al., 2015, 2017) which in turn could enhance their capacity to increase pH even as pH decreases over the next years. Our work strongly indicates the potential for seagrasses to mitigate low pH in coastal areas and has important implications for the conservation and management of seagrass ecosystems.

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CONFLICT OF INTEREST

The authors declare no conflicting interests.

AUTHOR CONTRIBUTIONS

Aurora M. Ricart, Melissa Ward, Tessa M. Hill, Eric Sanford, Kristy J. Kroeker, Yuichiro Takeshita, and Brian Gaylord conceived and designed methodology. Aurora M. Ricart, Melissa Ward, Kristy J. Kroeker, Yuichiro Takeshita, Sarah Merolla, Priya Shukla, and Aaron T. Ninokawa collected the data. Aurora M. Ricart, Brian Gaylord, Yuichiro Takeshita, Kristen Elsmore, and Aaron T. Ninokawa analyzed the data. Aurora M. Ricart led the writing of the manuscript. All authors contributed critically to the drafts and gave final approval for publication.

DATA AVAILABILITY STATEMENT

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supporting Information. Other not shown data are available on request from the corresponding author.

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REFERENCES

Barton, A., Hales, B., Waldbusser, G. G., Langdon, C., & Feelyd, R. A. (2012). The Pacific oyster, *Crassostrea gigas*, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects. *Limnology and Oceanography*, 57(3), 698–710. https://doi.org/10.4319/lo.2012.57.3.0698

Bates, D., Mächler, M., Bolker, B., & Walker, S. (2014). Fitting linear mixed-effects models using lme4. *Journal of Statistical Software*, 67(1), 1–48. https://doi.org/10.18637/jss.v067.i01

Bresnahan, P. J., Martz, T. R., Takeshita, Y., Johnson, K. S., & LaShomb, M. (2014). Best practices for autonomous measurement of seawater pH with the Honeywell Durafet. *Methods in Oceanography*, 9, 44–60. https://doi.org/10.1016/j.mio.2014.08.003

Buapet, P., Gullström, M., & Björk, M. (2013). Photosynthetic activity of seagrasses and macroalgae in temperate shallow waters can alter seawater pH and total inorganic carbon content at the scale of a coastal embayment. *Marine and Freshwater Research*, 64(11), 1040–1048. https://doi.org/10.1071/MF12124

Caldeira, K., & Wickett, M. E. (2003). Anthropogenic carbon and ocean pH. *Nature*, 425(6956), 365. https://doi.org/10.1038/425365a

Camp, E. F., Suggett, D. J., Gendron, G., Jompa, J., Manfrino, C., & Smith, D. J. (2016). Mangrove and seagrass beds provide different biogeochemical services for corals threatened by climate change. *Frontiers in Marine Science*, 3, 52. https://doi.org/10.3389/fmars.2016.00052

Clayton, T. D., & Byrne, R. H. (1993). Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Research Part I*, 40(10), 2115–2129. https://doi.org/10.1016/0967-0637(93)90048-8

Cyronak, T., Andersson, A. J., D'Angelo, S., Bresnahan, P., Davidson, C., Griffin, A., Kindeberg, T., Pennise, J., Takeshita, Y., & White, M. (2018). Short-term spatial and temporal carbonate chemistry variability in two contrasting seagrass meadows: Implications for pH buffering capacities. *Estuaries and Coasts*, 41(5), 1282–1296. https://doi.org/10.1007/s12237-017-0356-5

Cyronak, T., Takeshita, Y., Courtney, T. A., DeCarlo, E. H., Eyre, B. D., Kline, D. I., Martz, T., Page, H., Price, N. N., Smith, J., Stoltenberg, L., Tresguerres, M., & Andersson, A. J. (2020). Diel temperature and pH variability scale with depth across diverse coral reef habitats. *Limnology and Oceanography Letters*, 5(2), 193–203. https://doi.org/10.1002/lol2.10129

Dickson, A. G. (1990). Standard potential of the reaction: AgCl(s). + $\frac{1}{2}H_2(g)$ = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO_4^- in synthetic sea water from 273.15 to 318.15 K. *The Journal of Chemical Thermodynamics*, 22(2), 113–127. https://doi.org/10.1016/0021-9614(90)90074-Z

Duarte, C. M., & Cebrián, J. (1996). The fate of marine autotrophic production. *Limnology and Oceanography*, 41(8), 1758–1766. https://doi.org/10.4319/lo.1996.41.8.1758

Duarte, C. M., Hendriks, I. E., Moore, T. S., Olsen, Y. S., Steckbauer, A., Ramajo, L., Carstensen, J., Trotter, J. A., & McCulloch, M. (2013). Is ocean acidification an open-ocean syndrome? understanding anthropogenic impacts on seawater pH. *Estuaries and Coasts*, 36(2), 221–236. https://doi.org/10.1007/s12237-013-9594-3

Feely, R. A., Alin, S. R., Carter, B., Bednaršek, N., Hales, B., Chan, F., Hill, T. M., Gaylord, B., Sanford, E., Byrne, R. H., Sabine, C. L., Greeley, D., & Juranek, L. (2016). Chemical and biological impacts of ocean acidification along the west coast of North America. *Estuarine, Coastal and Shelf Science*, 183, 260–270. https://doi.org/10.1016/j.ecss.2016.08.043

Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Ianson, D., & Hales, B. (2008). Evidence for upwelling of corrosive "acidified" water onto the continental shelf. *Science*, 320(5882), 1490–1492. https://doi.org/10.1126/science.1155676

Fourqurean, J., Duarte, C. M., Kennedy, H., Marbà, N., Holmer, M., Mateo, M. A., Apostolaki, E. T., Kendrick, G. A., Krause-Jensen, D., McGlathery, K. J., & Serrano, O. (2012). Seagrass ecosystems as a globally significant carbon stock. *Nature Geoscience*, 5, 505–509. https://doi.org/10.1038/NGEO1477

Fourqurean, J. W., Moore, T. O., Fry, B., & Hollibaugh, J. T. (1997). Spatial and temporal variation in C:N: P ratios, ^{15}N, and ^{13}C of eelgrass *Zostera marina* as indicators of ecosystem processes, Tomales Bay, California, USA. *Marine Ecology Progress Series*, 157, 147–157. https://doi.org/10.3354/meps157147

Frankignoulle, M., & Distèche, A. (1984). CO_2 chemistry in the water column above a *Posidonia* seagrass bed and related air-sea exchanges. *Oceanologica Acta*, 7(2).

García-Reyes, M., & Largier, J. L. (2012). Seasonality of coastal upwelling off central and northern California: New insights, including temporal and spatial variability. *Journal of Geophysical Research: Oceans*, 117(3), 1–17. https://doi.org/10.1029/2011JC007629

Gattuso, J. P., Epitalon, J. M., Lavigne, H., & Orr, J. (2019). seacarb: Seawater carbonate chemistry. *R Package Version 3.2.12.* https://cran.r-project.org/package=seacarb

Green, E. P., & Short, F. T. (2003). *World atlas of seagrasses.* In E. P. Green & F. T. Short (Ed.). University of California Press. https://doi.org/10.1515/BOT.2004.029

Groner, M. L., Burge, C. A., Cox, R., Rivlin, N. D., Turner, M., Van Alstyne, K. L., Wyllie-Echeverria, S., Bucci, J., Staudigel, P., & Friedman, C. S. (2018). Oysters and eelgrass: potential partners in a high pCO_2 ocean. *Ecology*, 99(8), 1802–1814. https://doi.org/10.1002/ecy.2393

Gruber, N., Hauri, C., Lachkar, Z., Loher, D., Frölicher, T. L., & Plattner, G. K. (2012). Rapid progression of ocean acidification in the California Current System. *Science*, 337(6091), 220–223. https://doi.org/10.1126/science.1216773

Hendriks, I. E., Olsen, Y. S., Ramajo, L., Basso, L., Steckbauer, A., Moore, T. S., Howard, J., & Duarte, C. M. (2014). Photosynthetic activity buffers ocean acidification in seagrass meadows. *Biogeosciences*, 11(2), 333–346. https://doi.org/10.5194/bg-11-333-2014

Hettinger, A., Sanford, E., Hill, T. M., Lenz, E. A., Russell, A. D., & Gaylord, B. (2013). Larval carry-over effects from ocean acidification persist in the natural environment. *Global Change Biology*, 19(11), 3317–3326. https://doi.org/10.1111/gcb.12307

Hiraishi, T., Krug, T., Tanabe, K., Srivastava, N., Baasansuren, J., Fukuda, M., & Troxler, T. G. (Eds). (2013). *IPCC 2014, 2013 Supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories: Wetlands.* IPCC.

Hofmann, G. E., Smith, J. E., Johnson, K. S., Send, U., Levin, L. A., Micheli, F., Paytan, A., Price, N. N., Peterson, B., Takeshita, Y., Matson, P. G., de Crook, E., Kroeker, K. J., Gambi, M. C., Rivest, E. B., Frieder, C. A., Yu, P. C., & Martz, T. R. (2011). High-frequency dynamics of ocean pH: A multi-ecosystem comparison. *PLoS One*, 6(12). https://doi.org/10.1371/journal.pone.0028983

Hurd, C. L. (2015). Slow-flow habitats as refugia for coastal calcifiers from ocean acidification. *Journal of Phycology*, 51(4), 599–605. https://doi.org/10.1111/jpy.12307

Invers, O., Zimmerman, R., Alberte, R., Pérez, M., & Romero, J. (2001). Inorganic carbon sources for seagrass photosynthesis: an experimental evaluation of bicarbonate use in species inhabiting temperate waters. *Journal of Experimental Marine Biology and Ecology*, 265, 203–217. http://www.sciencedirect.com/science/article/pii/S002209810100332X

IPCC. (2014). Climate change 2014: Synthesis report. In R. K. Pachauri & L. Meyer (Eds.), *Contribution of working groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change.* IPCC.

James, R. K., van Katwijk, M. M., van Tussenbroek, B. I., van der Heide, T., Dijkstra, H. A., van Westen, R. M., Pietrzak, J. D., Candy, A. S., Klees, R., Riva, R. E. M., Slobbe, C. D., Katsman, C. A., Herman, P. M. J., & Bouma, T. J. (2020). Water motion and vegetation control the pH dynamics in seagrass-dominated bays. *Limnology and Oceanography*, 65(2), 349–362. https://doi.org/10.1002/lno.11303

Kapsenberg, L., & Cyronak, T. (2019). Ocean acidification refugia in variable environments. *Global Change Biology*, 25(10), 3201–3214. https://doi.org/10.1111/gcb.14730

Kennedy, H., Beggins, J., Duarte, C. M., Fourqurean, J. W., Holmer, M., Marba, N., & Middelburg, J. J. (2010). Seagrass sediments as a global carbon sink: Isotopic constraints. *Global Biogeochemical Cycles*, 24, GB4026.

Koch, M., Bowes, G., Ross, C., & Zhang, X. H. (2013). Climate change and ocean acidification effects on seagrasses and marine macroalgae. *Global Change Biology*, 19(1), 103–132. https://doi.org/10.1111/j.1365-2486.2012.02791.x

Koweek, D. A., Zimmerman, R. C., Hewett, K. M., Gaylord, B., Giddings, S. N., Nickols, K. J., Ruesink, J. L., Stachowicz, J. J., Takeshita, Y., & Caldeira, K. (2018). Expected limits on the ocean acidification buffering potential of a temperate seagrass meadow. *Ecological Applications*, 28(7), 1694–1714. https://doi.org/10.1002/eap.1771

Krause-Jensen, D., Marbà, N., Sanz-Martin, M., Hendriks, I. E., Thyrring, J., Carstensen, J., Sejr, M. K., & Duarte, C. M. (2016). Long photoperiods sustain high pH in arctic kelp forests. *Science Advances*, 2(12). https://doi.org/10.1126/sciadv.1501938

Kroeker, K. J., Kordas, R. L., Crim, R., Hendriks, I. E., Ramajo, L., Singh, G. S., Duarte, C. M., & Gattuso, J. P. (2013). Impacts of ocean acidification on marine organisms: Quantifying sensitivities and interaction with warming. *Global Change Biology*, 19(6), 1884–1896. https://doi.org/10.1111/gcb.12179

Kroeker, K. J., Kordas, R. L., Crim, R. N., & Singh, G. G. (2010). Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. *Ecology Letters*, 13(11), 1419–1434. https://doi.org/10.1111/j.1461-0248.2010.01518.x

Lai, C. Z., DeGrandpre, M. D., & Darlington, R. C. (2018). Autonomous optofluidic chemical analyzers for marine applications: Insights from the Submersible Autonomous Moored Instruments (SAMI) for pH and pCO_2. *Frontiers in Marine Science*, 4, 1–11. https://doi.org/10.3389/fmars.2017.00438

Lowe, A. T., Bos, J., & Ruesink, J. (2019). Ecosystem metabolism drives pH variability and modulates long-term ocean acidification in the Northeast Pacific coastal ocean. *Scientific Reports*, 9(1), 1–11. https://doi.org/10.1038/s41598-018-37764-4

Lowe, A. T., Kobelt, J., Horwith, M., & Ruesink, J. (2019). Ability of eelgrass to alter oyster growth and physiology is spatially limited and offset by increasing predation risk. *Estuaries and Coasts*, 42, 743–754. https://doi.org/10.1007/s12237-018-00488-9

Lueker, T. J., Dickson, A. G., & Keeling, C. D. (2000). Ocean pCO_2 calculated from DIC, TA, and the Mehrbach equations for K1 and K2: Validation using laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry*, 70, 105–119.

Manzello, D. P., Enochs, I. C., Melo, N., Gledhill, D. K., & Johns, E. M. (2012). Ocean acidification refugia of the Florida reef tract. *PLoS One*, 7(7), 1–10. https://doi.org/10.1371/journal.pone.0041715

Martz, T. R., Carr, J. J., French, C. R., & DeGrandpre, M. D. (2003). A submersible autonomous sensor for spectrophotometric pH measurements of natural waters. *Analytical Chemistry*, 75(8), 1844–1850. https://doi.org/10.1021/ac020568l

Martz, T. R., Connery, J. G., & Johnson, K. S. (2010). Testing the Honeywell Durafet for seawater pH applications. *Limnology and Oceanography: Methods*, 8(MAY), 172–184. https://doi.org/10.4319/lom.2010.8.172

Middelboe, A. L., & Hansen, P. J. (2007). High pH in shallow-water macroalgal habitats. *Marine Ecology Progress Series*, 338, 107–117.

Miller, J. J., Maher, M., Bohaboy, E., Friedman, C. S., & McElhany, P. (2016). Exposure to low pH reduces survival and delays development in early life stages of Dungeness crab (*Cancer magister*). *Marine Biology*, 163(5), 1–11. https://doi.org/10.1007/s00227-016-2883-1

Newman, W. (1979). Californian transition zone: significance of short-range endemics. In J. Gray & A. Boucot (Eds.), *Historical biogeography, plate tectonics, and the changing environment* (pp. 399–416). Oregon State University Press.

Newton, J. A., Feely, R. A., Jewett, E. B., Williamson, P., & Mathis, J. (2014). Global Ocean Acidification Observing Network: Requirements and governance Plan. *Global Ocean Acidification Observing Network*, *First edition*. www.iaea.org/ocean-acidification

Nielsen, K. J., Stachowicz, J. J., Carter, H., Boyer, K., Bracken, M., Chan, F., Chavez, F., Hovel, K., Kent, K., Nickols, K., Ruesink, J., Tyburczy, J., & Wheeler, S. (2018). *Emerging understanding of the potential role of seagrass and kelp as an ocean acidification management tool in California. California Ocean Science Trust, Oakland, California, USA.* (Issue January). www.oceansciencetrust.org

Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.

G., Plattner, G.-K., Rodgers, K. B., … Yool, A. (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature*, *437*(7059), 681–686. https://doi.org/10.1038/nature04095

Osborne, E. B., Thunell, R. C., Gruber, N., Feely, R. A., & Benitez-Nelson, C. R. (2020). Decadal variability in twentieth-century ocean acidification in the California Current Ecosystem. *Nature Geoscience*, *13*(1), 43–49. https://doi.org/10.1038/s41561-019-0499-z

Pacella, S. R., Brown, C. A., Waldbusser, G. G., Labiosa, R. G., & Hales, B. (2018). Seagrass habitat metabolism increases short-term extremes and long-term offset of CO_2 under future ocean acidification. *Proceedings of the National Academy of Sciences of the United States of America*, *115*(15), 3870–3875. https://doi.org/10.1073/pnas.1703445115

Perez, F. F., & Fraga, F. (1987). Association constant of fluoride and hydrogen ions in seawater. *Marine Chemistry*, *21*(2), 161–168. https://doi.org/10.1016/0304-4203(87)90036-3

Pierrot, D. E. L., & Wallace, D. W. R. (2006). *MS Excel Program Developed for CO_2 System Calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center. Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.* https://doi.org/10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a

Rivest, E. B., O'Brien, M., Kapsenberg, L., Gotschalk, C. C., Blanchette, C. A., Hoshijima, U., & Hofmann, G. E. (2016). Beyond the benchtop and the benthos: Dataset management planning and design for time series of ocean carbonate chemistry associated with Durafet-based pH sensors. *Ecological Informatics*, *36*, 209–220. https://doi.org/10.1016/j.ecoinf.2016.08.005

Saderne, V., Baldry, K., Anton, A., Agustí, S., & Duarte, C. M. (2019). Characterization of the CO_2 system in a coral reef, a seagrass meadow, and a mangrove forest in the central Red Sea. *Journal of Geophysical Research: Oceans*, *2*, 1–16. https://doi.org/10.1029/2019JC015266

Saderne, V., Fietzek, P., & Herman, P. M. J. (2013). Extreme variations of pCO_2 and pH in a macrophyte meadow of the Baltic Sea in summer: Evidence of the effect of photosynthesis and local upwelling. *PLoS One*, *8*(4), 2–9. https://doi.org/10.1371/journal.pone.0062689

Sand-Jensen, K., Binzer, T., & Middelboe, A. L. (2007). Scaling of photosynthetic production of aquatic macrophytes: A review. *Oikos*, *116*(2), 280–294.

Scanes, E., Scanes, P. R., & Ross, P. M. (2020). Climate change rapidly warms and acidifies Australian estuaries. *Nature Communications*, *11*(1), 1–11. https://doi.org/10.1038/s41467-020-15550-z

Seidel, M. P., DeGrandpre, M. D., & Dickson, A. G. (2008). A sensor for in situ indicator-based measurements of seawater pH. *Marine Chemistry*, *109*(1–2), 18–28. https://doi.org/10.1016/j.marchem.2007.11.013

Semesi, I., Beer, S., & Björk, M. (2009). Seagrass photosynthesis controls rates of calcification and photosynthesis of calcareous macroalgae in a tropical seagrass meadow. *Marine Ecology Progress Series*, *382*, 41–48. https://doi.org/10.3354/meps07973

Serrano, O., Lovelock, C. E., B. Atwood, T., Macreadie, P. I., Canto, R., Phinn, S., Arias-Ortiz, A., Bai, L. E., Baldock, J., Bedulli, C., Carnell, P., Connolly, R. M., Donaldson, P., Esteban, A., Ewers Lewis, C. J., Eyre, B. D., Hayes, M. A., Horwitz, P., Hutley, L. B., … Duarte, C. M. (2019). Australian vegetated coastal ecosystems as global hotspots for climate change mitigation. *Nature Communications*, *10*(1), 1–10. https://doi.org/10.1038/s41467-019-12176-8

Silbiger, N. J., & Sorte, C. J. B. (2018). Biophysical feedbacks mediate carbonate chemistry in coastal ecosystems across spatiotemporal gradients. *Scientific Reports*, *8*(1), 1–11. https://doi.org/10.1038/s41598-017-18736-6

Su, J., Cai, W.-J., Brodeur, J., Chen, B., Hussain, N., Yao, Y., Ni, C., Testa, J. M., Li, M., Xie, X., Ni, W., Scaboo, K. M., Xu, Y.-Y., Cornwell, J., Gurbisz, C., Owens, M. S., Waldbusser, G. G., Dai, M., & Kemp, W. M. (2020). Chesapeake Bay acidification buffered by spatially decoupled carbonate mineral cycling. *Nature Geoscience*, *13*(6), 441–447. https://doi.org/10.1038/s41561-020-0584-3

Takeshita, Y., Jones, B. D., Johnson, K. S., Chavez, F. P., Rudnick, D. L., Blum, M., Conner, K., Jensen, S., Long, J. S., Maughan, T., Mertz, K. L., Sherman, J. T., & Warren, J. K. (2021). Accurate pH and O_2 measurements from spray underwater gliders. *Journal of Atmospheric and Oceanic Technology*, *38*(2), 181–195. https://doi.org/10.1175/jtech-d-20-0095.1

Takeshita, Y., Martz, T. R., Johnson, K. S., & Dickson, A. G. (2014). Characterization of an ion sensitive field effect transistor and chloride ion selective electrodes for pH measurements in seawater. *Analytical Chemistry*, *86*(22), 11189–11195. https://doi.org/10.1021/ac502631z

Thomas, S. (2014). Blue carbon: Knowledge gaps, critical issues, and novel approaches. *Ecological Economics*, *107*, 22–38. https://doi.org/10.1016/j.ecolecon.2014.07.028

Thomsen, J., Haynert, K., Wegner, K. M., & Melzner, F. (2015). Impact of seawater carbonate chemistry on the calcification of marine bivalves. *Biogeosciences*, *12*(14), 4209–4220. https://doi.org/10.5194/bg-12-4209-2015

Unsworth, R. K. F., Collier, C. J., Henderson, G. M., & McKenzie, L. J. (2012). Tropical seagrass meadows modify seawater carbon chemistry: Implications for coral reefs impacted by ocean acidification. *Environmental Research Letters*, *7*(2). https://doi.org/10.1088/1748-9326/7/2/024026

Wahl, M., Schneider Covachã, S., Saderne, V., Hiebenthal, C., Müller, J. D., Pansch, C., & Sawall, Y. (2018). Macroalgae may mitigate ocean acidification effects on mussel calcification by increasing pH and its fluctuations. *Limnology and Oceanography*, *63*(1), 3–21. https://doi.org/10.1002/lno.10608

Waldbusser, G. G., Brunner, E. L., Haley, B. A., Hales, B., Langdon, C. J., & Prahl, F. G. (2013). A developmental and energetic basis linking larval oyster shell formation to acidification sensitivity. *Geophysical Research Letters*, *40*(10), 2171–2176. https://doi.org/10.1002/grl.50449

Waldbusser, G. G., Hales, B., Langdon, C. J., Haley, B. A., Schrader, P., Brunner, E. L., Gray, M. W., Miller, C. A., & Gimenez, I. (2015). Saturation-state sensitivity of marine bivalve larvae to ocean acidification. *Nature Climate Change*, *5*(3), 273–280. https://doi.org/10.1038/nclimate2479

Waldbusser, G. G., & Salisbury, J. E. (2014). Ocean acidification in the coastal zone from an organism's perspective: multiple system parameters, frequency domains, and habitats. *Annual Review of Marine Science*, *6*(1), 221–247. https://doi.org/10.1146/annurev-marine-121211-172238

Zimmerman, R. C., Hill, V. J., & Gallegos, C. L. (2015). Predicting effects of ocean warming, acidification, and water quality on Chesapeake region eelgrass. *Limnology and Oceanography*, *60*(5), 1781–1804. https://doi.org/10.1002/lno.10139

Zimmerman, R. C., Hill, V. J., Jinuntuya, M., Celebi, B., Ruble, D., Smith, M., Cedeno, T., & Swingle, W. M. (2017). Experimental impacts of climate warming and ocean carbonation on eelgrass *Zostera marina*. *Marine Ecology Progress Series*, *566*, 1–15. https://doi.org/10.3354/meps12051

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