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Tidal, Geological, and Biological Impacts to Humboldt Bay's pH

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This research examines factors that control pH in Humboldt Bay – a shallow, tidally-driven estuary in northern California (USA) that supports shellfisheries which are economically important to the state. Time-series data from hydrographic sensors at two Central and Northern California Ocean Observing System (CenCOOS) stations, as well as sediment incubations, were used to understand the role of tides, biological productivity, and carbonate dissolution in controlling pH on various timescales. Differences in pH, dissolved oxygen, chlorophyll, and temperature between an in-bay sensor and a coastal sensor indicate that the tidal flux exerts a long-term, seasonal control on pH, but biological productivity substantially modifies carbon and oxygen, thereby controlling pH on daily and weekly timescales. Sediment samples were also collected from the bay in 2021 to study carbonate dissolution. Sediments were incubated for three days in both stirred and unstirred conditions (to mimic tidal mixing and no tidal mixing respectively) and DO, pH and alkalinity were monitored. For all stirred incubations, large increases in pH and alkalinity suggested considerable carbonate sediment dissolution. When scaled to the bay's in-situ suspended sediment concentrations, carbonate dissolution may exert a supplementary control on pH at similar time scales as biological productivity, but the magnitude of its effect is less.

Introduction

Ocean acidification occurs in response to increased anthropogenic emissions of carbon dioxide (CO2). Rising CO2 in the atmosphere increases dissolved CO2 in the ocean. This forms carbonic acid (Eqn 1) which then dissociates to bicarbonate and H+, lowering the pH (Eqn 2) (Feely et al., 2009). Data compiled since the 1980s at two Atlantic marine stations confirm that ocean pH has dropped by 0.02 every decade in response to increased atmospheric CO2 (Doney et al., 2009; Feely et al., 2009; Gattuso & Hansson, 2011).

Eqn. 1) CO_2 (atm) + $H_2O \Leftrightarrow H_2CO_3$ (aq)

Eqn. 2) $H_2CO_3 \Leftrightarrow H+ + HCO_3- \Leftrightarrow 2H+ + CO^2{}_3{}^-$

More dissolved CO2 shifts the equilibrium toward bicarbonate from both directions in Eqn 2. So a related consequence of high-CO2 in the ocean is the resulting reduction in carbonate ion (CO32-). Many marine organisms rely on CO32- for building calcium carbonate shells, and will struggle to build shells in a high-CO2 environment. In upwelling regions, conditions are particularly challenging since calcifying organisms must contend with higher atmospheric CO2 from "above" and the already high-CO2 water which naturally upwells from "below". During upwelling, many calcifying heterotrophs are already facing undersaturated conditions with respect to aragonite, a common form of calcium carbonate found in a number of important zooplankton and juvenile shellfish like oysters, red sea urchins and crab (Fabry et al., 2008; Feely et al., 2009; Rassmann et al., 2018). Even calcifying primary producers, which can initially benefit from additional CO2 that promotes increased photosynthesis and thus more energy to form shells, will struggle to build shells once dissolved CO2 reaches high enough levels (Ries, 2011). Thus, increasing CO2 in the ocean raises important concerns for the commercial cultivation of shellfish, including oysters and clams (Lim et al., 2021).

Many estuarine ecosystems support ecologically and commercially important shellfish, and already face adverse impacts from ocean acidification (Fabry et al., 2008). Understanding the factors that control pH in estuarine environments is key to mitigate future impacts. But these factors are complicated and vary considerably from one region to another. For example, Feely et al. (2008) observed low aragonite saturation state in surface waters along the entire U.S. west coast, with the lowest values just off the coast of northern California, which they attributed to a combined effect of upwelling and anthropogenic CO2. Further north in Puget Sound, WA, Feely et al. (2010) found that low pH was controlled by several factors including: the tidal input of acidified coastal waters, restricted circulation within the sound, and local respiration of organic matter. They estimated the tidal input of coastal waters was responsible for 24 - 49% of the acidified waters in the sound. Another factor found to control pH in bays and inlets along the west coast is eelgrass, which was found to significantly mitigate ocean acidification (Ricart et al., 2021; Werblow & Cobo y Gonzales, 2020). Ricart et al. (2021) found most eelgrass meadows contribute to at least a +0.1 increase in pH (equivalent to a 30% reduction in H+), but the increase was stronger in higher latitude meadows than in lower latitudes. Additionally, carbonate sediments have been found to control pH in estuarine environments. In both field (Su et al., 2020) and modeling studies (Shen et al., 2019) calcium carbonate dissolution from suspended sediments was found to mitigate the acidifying impacts of aerobic respiration and anthropogenic CO2 dissolution in Chesapeake Bay.

Ultimately the control of pH within a given estuary will depend on its physical, biological and geological characteristics. In this study, we examine pH and other related factors in Humboldt Bay, CA (HB). As a semi-enclosed, shallow bay, whose circulation is strongly controlled by the tides (Barnhart et al., 1992), HB provides an opportunity to assess tidal inputs as the primary control on pH. In addition, the bay is home to a thriving eelgrass community which contributes substantially to primary productivity, and provides habitat and detritus for a broad host of heterotrophic zooplankton and commercially important shellfish like oysters and crab (Schlosser & Eicher, 2012). Finally, the bay has a small load of carbonate sediments which can be resuspended by tidal mixing and alter pH through the carbonate equilibrium in seawater.

Since the tides, sediments, and biology have been shown to have competing and complementary impacts on the pH of other estuaries, our goal in this study was to determine which of these processes are most critical in controlling the pH in HB. In particular we address the following hypotheses:

1) Humboldt Bay's pH is driven by the tidal influx from coastal waters. This influx is the forcing for the pH in the bay that is brought in with each tidal cycle and is modified only as the nearshore waters change.
2) Humboldt Bay's pH is driven by carbonate sediment dissolution. Resuspension of carbonate sediments will promote dissolution of carbonate, which will raise pH as the released carbonate reacts with H^+.
3) Humboldt Bay's pH is driven by biological productivity and respiration. The prevalence of eelgrass beds and phytoplankton will raise the pH above the tidal forcing during periods of photosynthesis; while heterotrophic respiration or shell-building by marine calcifiers will lower the pH below the tidal forcing.

Site Description

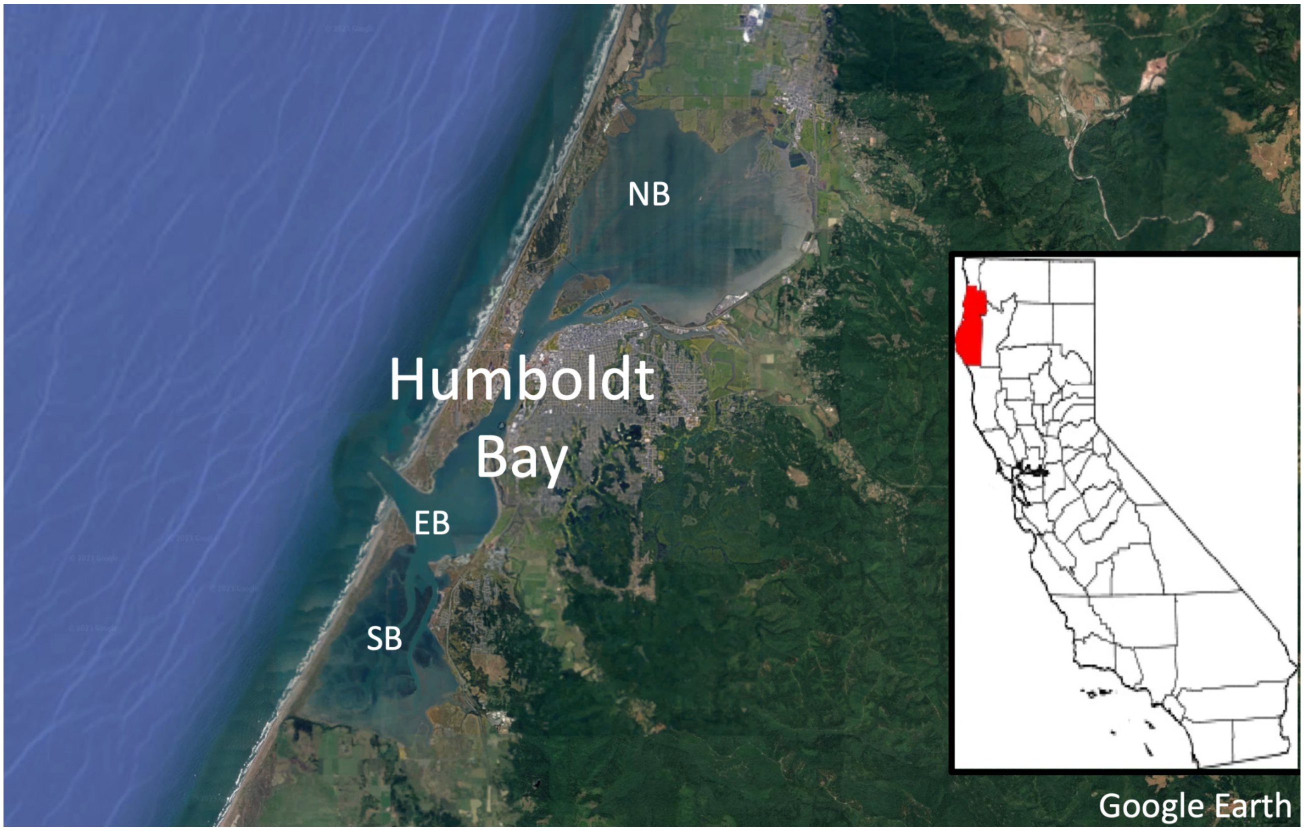
HB is located on northern California's coast in Humboldt County, CA (USA) (Figure 1). It is a semi-enclosed basin, connected to the Pacific Ocean by a narrow entrance channel. HB is 22.5 km long, up to 6.9 km wide, and spans 28.0 - 62.4 km^2 from mean low to mean high tide (Schlosser & Eicher, 2012). Mean volume is increasing slowly with time due to an estimated sea level rise of 47.2 cm/century (Sullivan et al., 2022). HB comprises three distinct basins: the northernmost known as North Bay (NB); the central channel known as Entrance Bay (EB); and the southernmost known as South Bay (SB) (Figure 1).

The climate in HB has two seasonal periods (Schlosser & Eicher, 2012). From October to April, the climate is mild and wet with frequent storms (Barnhart et al., 1992) and winds primarily out of the southwest (Claasen, 2003). From May to September, the climate is relatively cool and dry (Barnhart et al., 1992). Northerly winds cause intense upwelling starting in May and peaking in the summer, substantially altering the seawater that enters HB during flood tide.

HB circulation is strongly controlled by tides. HB has a large tidal prism, 44% in North Bay (NB), and 66% in South Bay (SB) (Schlosser & Eicher, 2012). Tidal currents are strongest in the channels, and decrease with distance from the entrance, while tidal amplitude increases with distance from the entrance (Schlosser & Eicher, 2012).

Tidal currents strongly influence the distribution of sediments in HB. Channels are dominated by sand; mudflats by silt & clay; marshes by peat (Schlosser & Eicher, 2012). Most of the sediments in HB come from the local drainage basin, which includes portions of the Klamath Mountains and the Coast Ranges (Barrett, 2004). Littoral sediments from coastal rivers to the north (Mad) and south (Eel) also enter HB during flood tide (Schlosser & Eicher, 2012). Although the mineralogy of the sediments is not well known, local field studies have found carbonate minerals present in NB and SB at weight percents from 0.5-1.0% (Bolster et al., 2015).

Figure 1.
A satellite image of Humboldt Bay (HB) in Humboldt County, CA (Google Earth, version 7.3.3.7786). The bay is nominally located at 40°46'N, 124°12'W and is composed of three distinct basins: North Bay (NB) sometimes referred to as Arcata Bay, Entrance Bay (EB), and South Bay (SB). Inset shows the location of Humboldt County in California.



A dominant biological feature of HB is eelgrass (*Zostera marina*), a marine plant mainly located in NB and SB, where water is retained in mudflats during low tide (Monroe et al., 1973). Satellite imagery indicates 22.85 km^2 of eelgrass across the entire bay, which is more than 30% of the coastal wetland habitat in HB (Schlosser & Eicher, 2012). Eelgrass affects the ecosystem extensively, including the sediment regime and infaunal distribution, (Barnhart et al., 1992; Moore et al., 2004)eelgrass (Zostera marina. It also alters dissolved oxygen (DO) and dissolved $CO_{2,}$ via photosynthesis, and turbidity and total dissolved solids via the production of organic matter and detritus (Gilkerson & Merkel, 2017).

Other major biological features in HB include phytoplankton and oysters. Phytoplankton are primarily advected with the tidal input and can then bloom within the bay. Like eelgrass, they are essential primary producers. Oysters are primarily cultured within the bay, with mariculture expanding from small areas in the 1950s (Monroe et al., 1973) to many acres of NB mudflats today. Oysters act as a source of dissolved CO_2 via their respiration and production of carbonate shells. They also provide a physical setting that acts as a sink, burying organic carbon, but also inorganic carbon, which in mudflats leads to a net venting of CO_2 (Fodrie et al., 2017).

Methods

To address our hypotheses, we utilized a combined data analysis and experimental approach. For hypotheses 1 and 3, we analyzed water quality data from two Central and Northern California Ocean Observing System (CenCOOS) stations: Chevron Dock in HB and Trinidad Pier about 15 miles north (Figure 2). We chose Chevron dock because it's centrally located in the bay, and Trinidad Pier because it monitors coastal waters similar to the waters entering HB on each flood tide.

CenCOOS sensors measure pH, temperature, depth, DO, turbidity, and chlorophyll-a (chl-a) at 15-minute intervals, with brief gaps of a few days for sensor calibration and maintenance. Data is quality controlled by CenCOOS technicians and faculty at Cal Poly Humboldt. We analyzed data from 2018 because it was the most recent year that had been fully quality controlled at the time of the study.

Data for each location was analyzed by comparing daily means and anomalies of pH to the other water quality parameters. Daily averages were first determined for all parameters. Monthly means were calculated from these daily averages, and anomalies were calculated by subtracting the monthly mean from each data point.

To address Hypothesis 2, bottom sediments were collected on 25 April 2021 at seven stations inside HB (Figure 3). A box corer or a Shipek grab was used to collect sediment, depending on the expected sediment type. Samples were collected at high slack tide, when the least amount of suspended sediment was expected, and the depth would allow the ship to access the sampling area.

Sediments were refrigerated in sealed Whirl-Pak bags for up to 2 weeks. They were then incubated at room temperature in Biological Oxygen Demand (BOD) bottles. For each incubation, 0.5 g of sediment was placed into 300 g of artificial seawater. Artificial seawater was prepared by adding sodium chloride to distilled deionized water to approximate HB's salinity of 33 ‰, and adding sodium bicarbonate and sodium carbonate to approximate 2000 μmol/kg of alkalinity. Samples were then incubated for three days under constant mixing using a magnetic stir plate (to mimic tidal mixing) or without stirring (to mimic no tidal mixing).

Incubations were periodically sampled for DO using a Hach optical DO probe, and for pH using a Hach glass electrode. Alkalinity was determined on replicate bottles by filtering 40 mL of incubation sample and analyzing using the Gran titration on a Metrohm 848 Titrino. A known mass of the sample was titrated with a standardized solution of dilute hydrochloric acid. pH was monitored after each addition of acid until a pH of 3.00 was reached. The measured pH versus volume was then graphically analyzed to identify the equivalence point and calculate the alkalinity. Only sediments from NB6, NB5, NB2, where eelgrass and oyster mariculture are most concentrated (Figure 4), and EB2, where tidal currents are greatest, were incubated (Figure 3).

Results

CeNCOOS Data Analysis

Daily average pH and temperature were strongly correlated at both Trinidad and HB. At Trinidad between April and November 2018, sharp decreases in temperature of 2-3°C were accompanied by sharp decreases in pH of 0.3-0.6 (Figure 5). Temperature and pH minima were followed by sharp increases on the same order of magnitude. Similar trends are observed in HB but of lesser magnitude. Temperature decreases in HB are 1-2°C between April and November, and the accompanying pH decreases are only 0.1-0.3. Temperature and pH were not as strongly correlated in July and August in HB.

The rapid decreases in temperature at Trinidad are indicators of coastal upwelling that brings cooler, higher-CO_2, lower-pH, and more nutrient-rich water to the surface within a few days (Gilkerson & Merkel, 2017). The rapid increase in temperature and pH that ensues after these events

Figure 2.
Chevron dock sensor in Humboldt Bay at 40.7775N, 124.1965W (left). Trinidad pier sensor along the northern California coast at 41.0550N, 124.1470W (right). Images are from Google Earth (version 7.3.3.7786). Trinidad is situated along the coast about 15 miles north of the Entrance Channel of Humboldt Bay

Figure 3.
Sediment sampling locations for R/V Coral Sea cruise on 25 April 2021. This image was generated using Google Earth (version 7.3.3.7786). Note the proximity of Station EB1 to Chevron Dock (Figure 2).

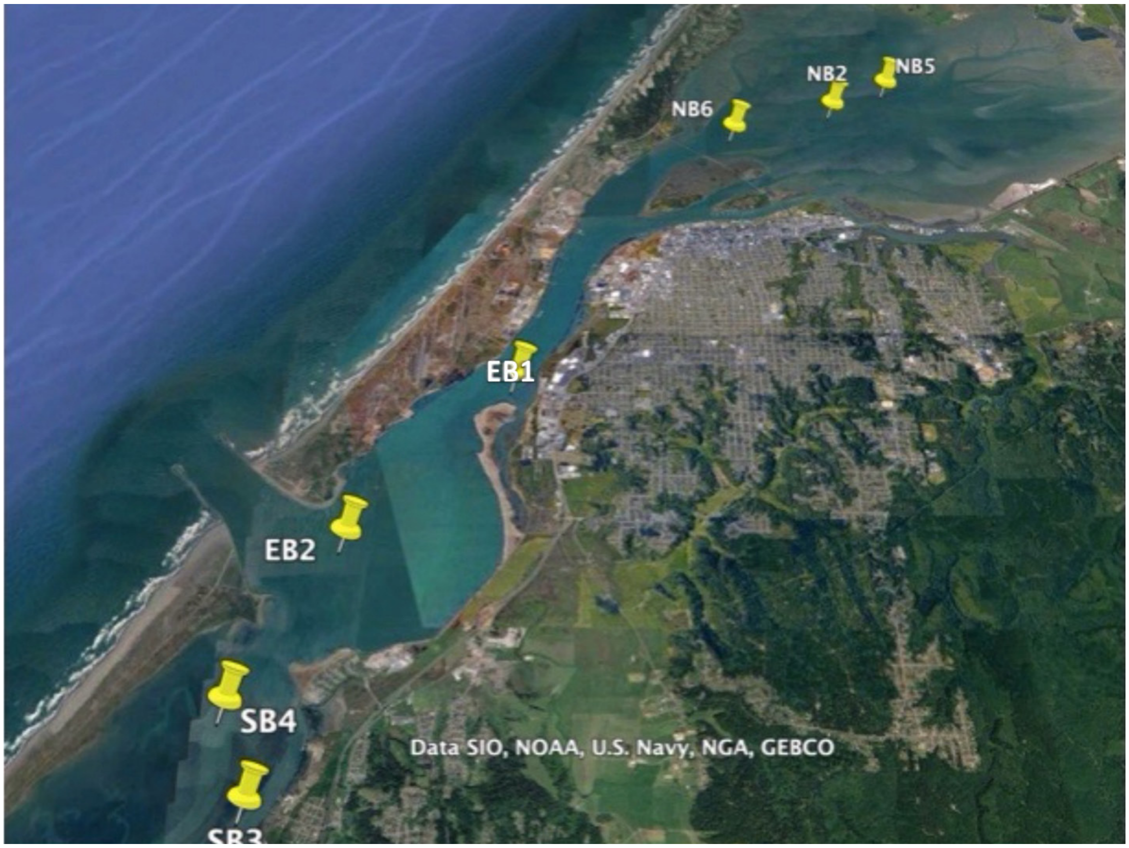
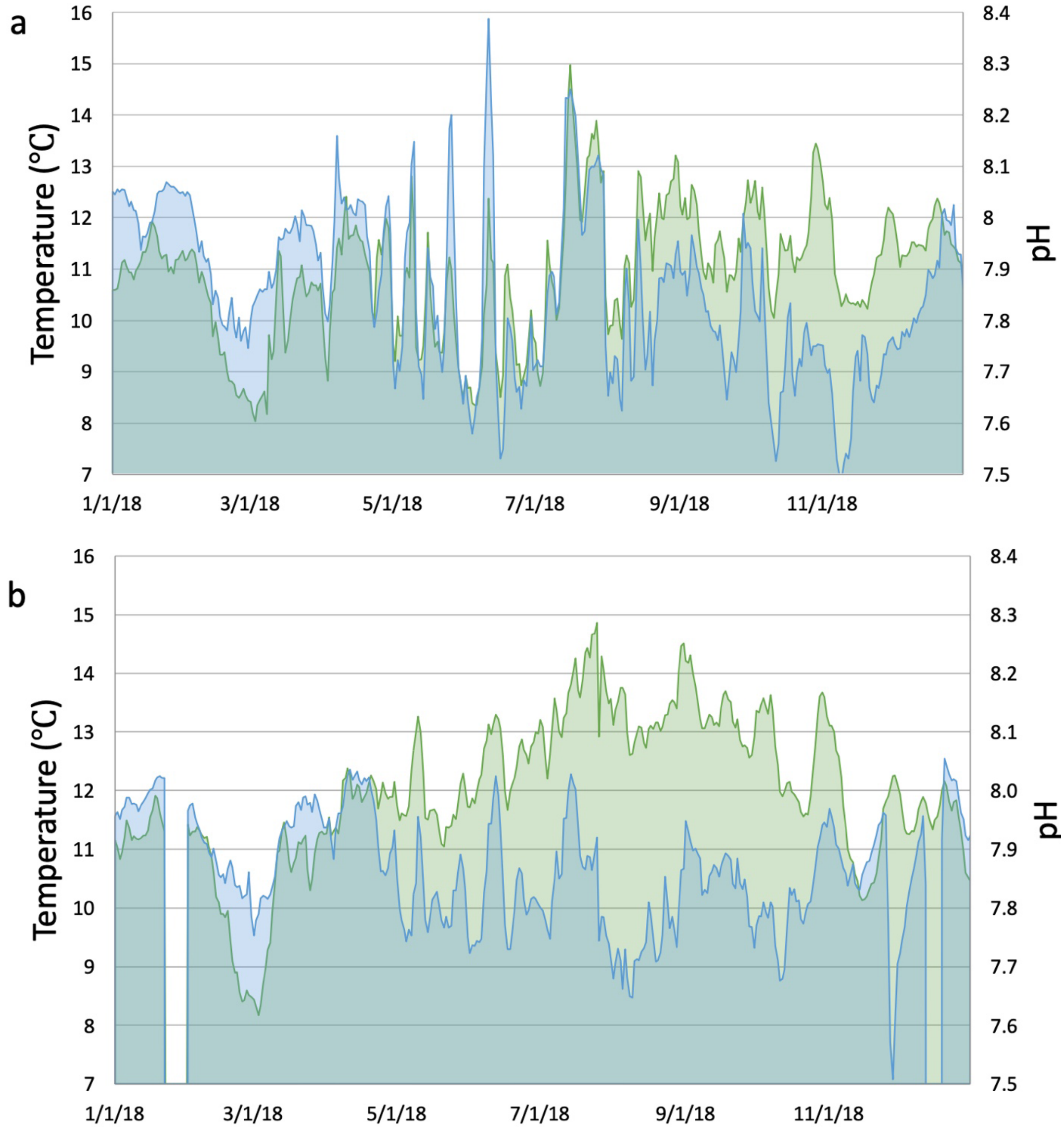


Figure 4.
Historical water quality stations indicating eelgrass rich patches and oyster mariculture locations (Google Earth, v. 7.3.3.7786). Eelgrass is indicated by the darker of the mudflats between channels. Oyster beds are generally found on the periphery of these patches adjacent to channels. Stations with an 'e' are centrally located in eelgrass beds. Stations with an 'o' are near oyster beds.

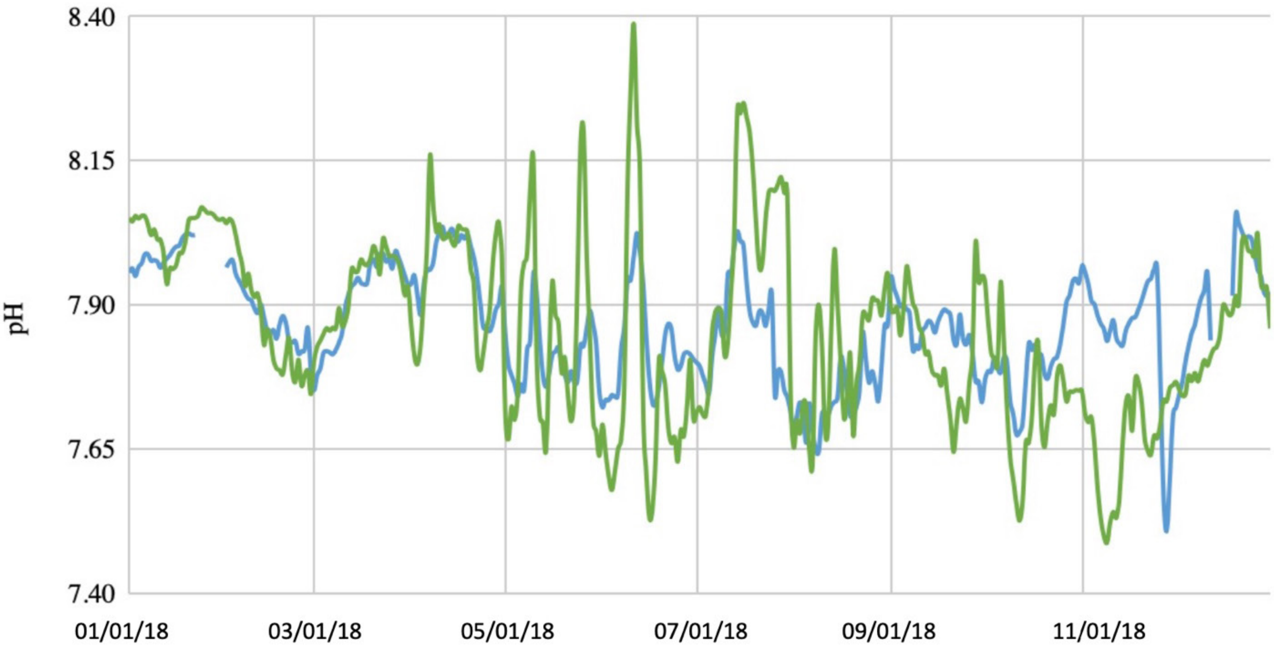
Figure 5.
pH (blue) and temperature (green) for 2018 at Chevron Dock in Humboldt Bay (a) and Trinidad pier (b). Individual points represent the mean of all 15-minute interval measurements collected during a day. Periods in late January (for both pH and temp) and in mid-December (for pH) reflect times when the sensor was not collecting data due to calibration and maintenance.



indicates relaxation periods: as the vertical circulation slows, the atmosphere warms the surface water, and phytoplankton accumulate, drawing down CO_2 and raising the pH.

Within HB the upwelling/relaxation cycle is also evident but the impact on pH is muted. Comparing pH at Trinidad and HB (Figure 6), we see that Trinidad pH minima are more frequent and of longer duration. Using a threshold pH of 7.8 – established by Feely et al. (2009) as a threshold for the saturation state of aragonite – Trinidad drops below the threshold 20 times during the year, for an average of 7 days per drop. In contrast, HB drops below the threshold only 15 times, for an average of 6 days per drop. This suggests that processes within HB may buffer the acidified coastal waters that enter with the tides. HB also exhibits less extreme

Figure 6.
pH in Humboldt Bay (blue) and at Trinidad (green) for 2018. Data were obtained from CenCOOS sensors which are continuously deployed at each site to collect pH and depth data every 15 minutes. Periods in late January and in mid-December reflect times when the sensor was not collecting data due to calibration and maintenance.



maxima than Trinidad. Trinidad exceeds the 7.8 threshold 19 times during the year, for an average of 8 days; while HB exceeds the threshold only 16 times, but stays above the threshold for an average of 13 days. Overall HB experiences more total days above the threshold during the year, but the maximum pH during these periods is lower than at Trinidad. This suggests that the relaxation period between upwelling events elicits a longer but less intense biological response within HB.

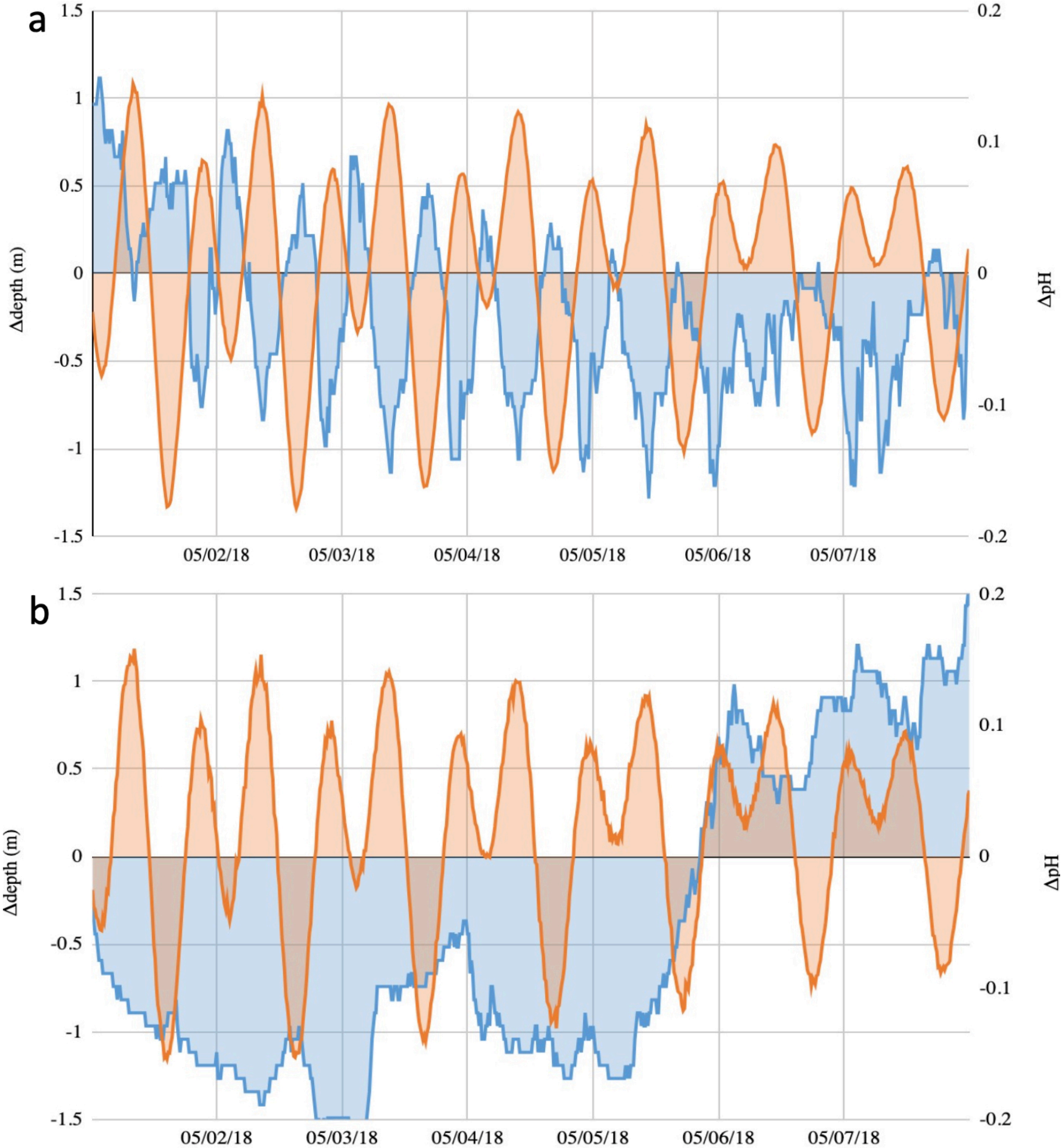
There is a clear correlation between the pH and depth anomalies within HB (Figure 7a). Generally, when the depth increases, indicating a flood tide, the pH decreases. When the depth decreases, indicating an ebb tide, the pH increases. Although this trend is true for most of the 2018 dataset, there are periods where the pH and depth increase and decrease synchronously (Figure 8). These periods show an inverse correlation between HB's pH and the tides. This pattern is determined by the relative pH of the coastal waters (indicated by Trinidad) and that of HB. When the pH in HB is greater than Trinidad, there is a decrease in pH with the incoming tide; when the pH in HB is less than Trinidad, there is an increase with the incoming tide (Figure 6).

The pattern at Trinidad demonstrates a pH which is not controlled by the tidal cycle (Figure 7b). The depth, an indicator of the tide, changes frequently without noticeable changes to the pH. The pH variation at Trinidad appears to be predominantly controlled by upwelling events, as indicated by the strong correlation with temperature (Figure 5b).

pH and DO demonstrate strong correlation in both HB and Trinidad (Figure 9). Examining one week in May where upwelling was prevalent at the start of the week, the pH anomalies in HB increase in accordance with the DO anomalies: reaching +0.1 when DO % saturation reaches +10%; and dropping to -0.1 when DO % saturation reaches -20%. At Trinidad, pH anomalies reach +0.2 when DO % saturation reaches +20%; -0.2 when DO % saturation reaches -20%. These correlations suggest a biological alteration of pH and DO. Positive anomalies imply increased primary productivity, which raises DO and reduces CO_2, raising pH. Negative anomalies imply increased respiration, which reduces DO and increases CO_2, lowering pH.

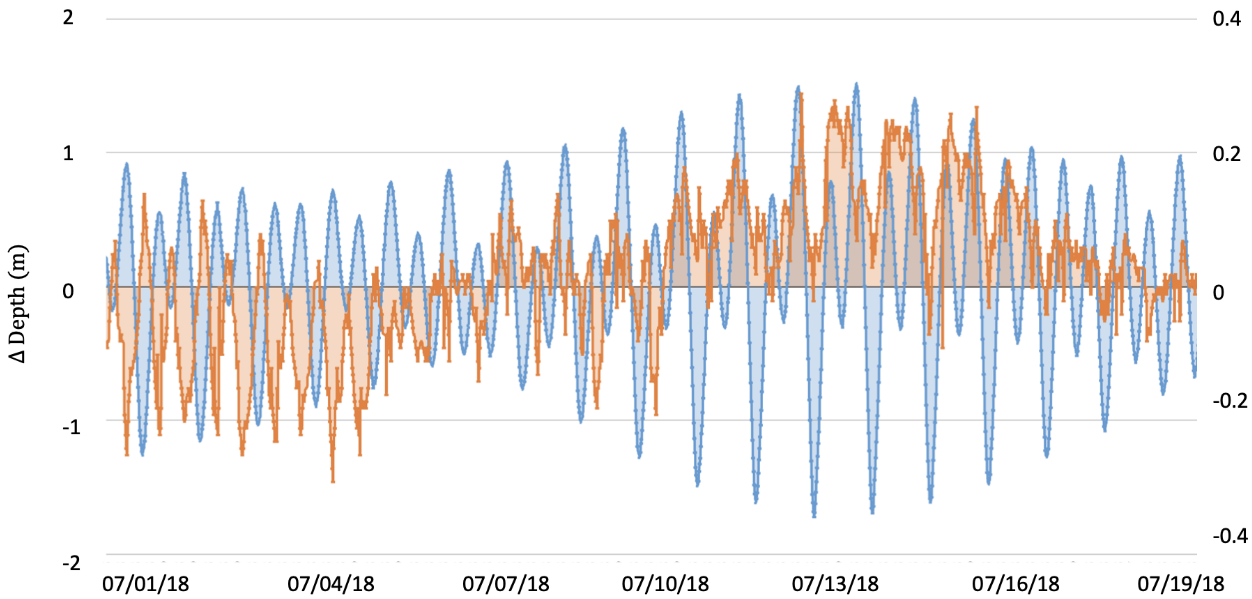
At Trinidad the negative DO and pH anomalies that lead off this week in May are indicators of upwelling. In contrast, during the same part of the week in HB, positive anomalies in pH and DO are observed. This implies that DO and pH are being elevated relative to the coastal water that enters HB during upwelling. Increased primary productivity is again the likely culprit: raising DO and pH as phytoplankton access the high-nutrient water that enters the bay. As upwelling continues in the first few days of May, DO and pH oscillate with each tidal cycle but edge toward the coastal water values observed at Trinidad. Then, as upwelling subsides in the last

Figure 7.
pH anomaly (blue) and depth anomaly (orange) (an indicator of tidal amplitude) from the first week of May 2018 at Chevron Dock in Humboldt Bay (a) and Trinidad Pier (b). Data were obtained from CenCOOS sensors which are continuously deployed at each site to collect pH and depth data every 15 minutes. Anomalies were calculated by subtracting the monthly mean from each value.



few days of the week, there is a large positive anomaly in both pH and DO at Trinidad, which is about twice as large as what was observed in HB earlier in the week. Conversely in HB at this time a negative anomaly in DO and pH is observed. This suggests that Trinidad's biological response to upwelled waters is stronger than the response in HB. It could also indicate that during periods of relaxation, primary production in HB shifts rapidly toward net respiration. This results in a lower pH and DO in HB when productivity in the coastal waters kicks into high gear. Over subsequent tidal cycles this coastal water signature will get progressively mixed into HB, but the magnitude of the signal is ultimately

Figure 8.
pH anomaly (blue) and depth anomaly (orange) (an indicator of tidal amplitude) from the first part of July 2018 at Chevron Dock in Humboldt Bay. Data were obtained from CenCOOS sensors which are continuously deployed at each site to collect pH and depth data every 15 minutes. Anomalies were calculated by subtracting the monthly mean from each value. Note that the first week was during an upwelling event, followed by a relaxation period.



controlled by the balance between primary productivity and respiration in HB.

The relationship between pH and chl-a at HB and Trinidad provide further support for the biological control of pH (Figure 10). Chl-a anomalies above 5 mg/m^3 generally indicate a phytoplankton bloom. At Trinidad two blooms are evident starting May 6th and 25th, with an additional bloom possibly on the 16th. (The May 6th bloom is coincident with the upwelling/relaxation pattern in Figures 7 & 9). pH generally rises with each bloom due to an increase in primary productivity, but the increase in pH precedes the May 6th bloom by a few days. This could be due to an initial increase in primary productivity per phytoplankton cell, which precedes the increase in cell numbers, or to enhanced grazing by zooplankton. It might also be due to continued upwelling during the bloom, advecting phytoplankton offshore by Ekman transport. These factors are not consistent, as pH and chl-a increase nearly synchronously during the May 25th bloom.

In HB the same three blooms are evident. and the chl-a has a similar variability as at Trinidad (Figure 10a). The anomalies oscillate with the tidal cycle, but generally maintain a timing consistent with Trinidad. The pH also increases with chl-a, as photosynthesis draws down CO_2 and raises pH. The correlation between pH and chl-a further emphasizes the control of biological processes on pH in HB.

Incubation Data Analysis

For each sediment incubation, DO decreased over time (Figure 11). Over the 3-day period, mixed incubations ranged from a 14.1 μmol/kg decrease at EB2 to a 36.7 μmol/kg decrease at NB2. Average decrease across all sites was 28.6 μmol/kg. Over the same period, unmixed incubations ranged from a 4.7 μmol/kg decrease at EB2 to a 24.0 μmol/kg decrease at NB5. Average decrease in DO across all sites was 13.6 μmol/kg for these unmixed incubations.

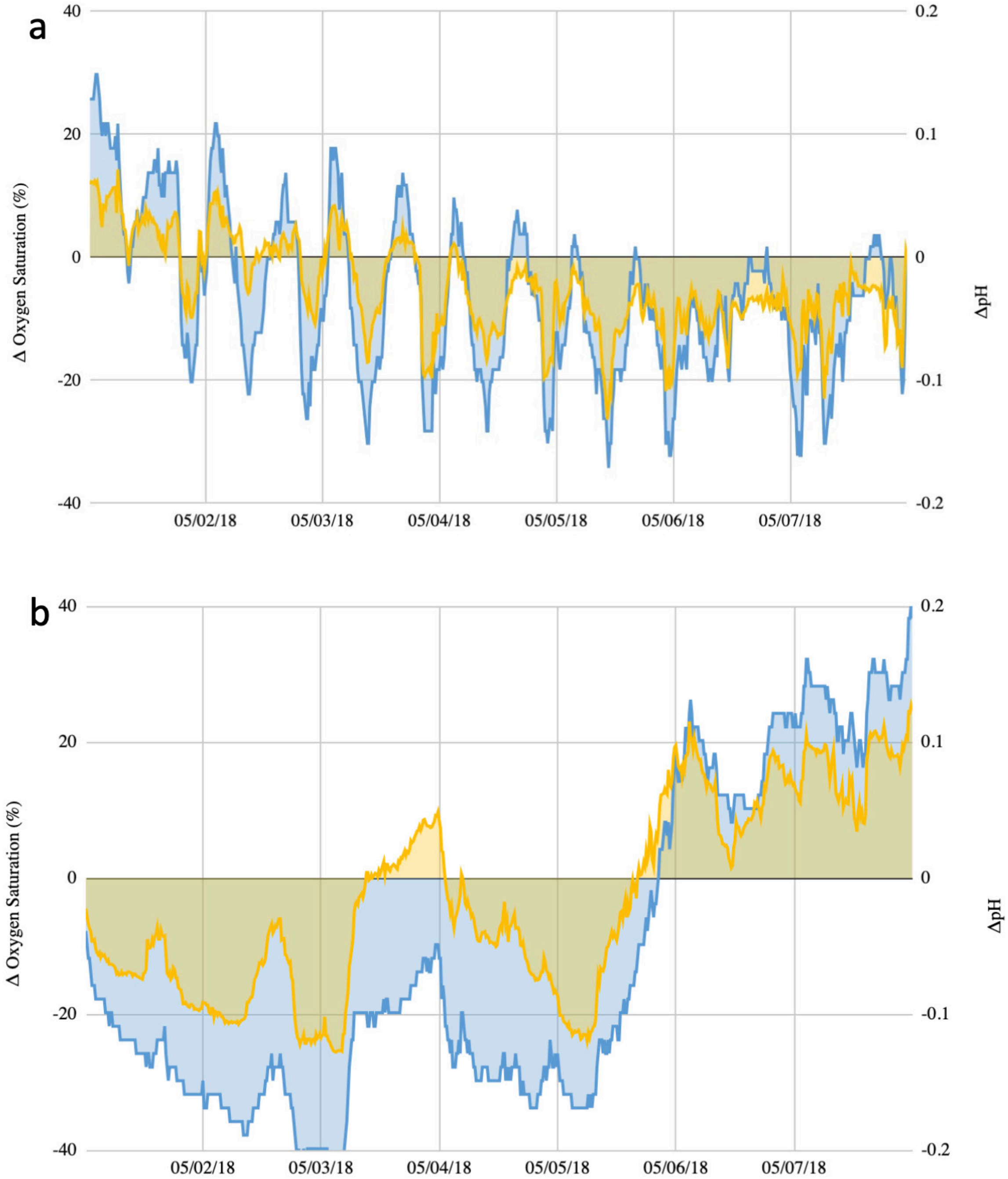
There was an average increase in pH of 0.62 for the mixed incubations from the initial day (0 hours) to the final day (72 hours) (Figure 11). The greatest increase in pH was 0.98 for station NB6. The smallest increase in pH was 0.31 for station NB5.

There was no clear trend in pH for the unmixed incubations. While the pH for station NB6 slightly increased by 0.06, there was an average decrease in pH of 0.06 for stations NB5 and NB2. Station EB2 did not experience any change in pH between the initial and final days.

The increasing trend in pH throughout all stations for the mixed incubations indicates that mixing enhanced the dissolution of calcium carbonate within the sediments. As the calcium carbonate dissolved, carbonate ions bonded with H^+ to produce bicarbonate (Eqn 2), raising the pH.

Three blank BOD bottles were measured on the initial day (0 hour) to obtain an average starting alkalinity of 1953 μmol/

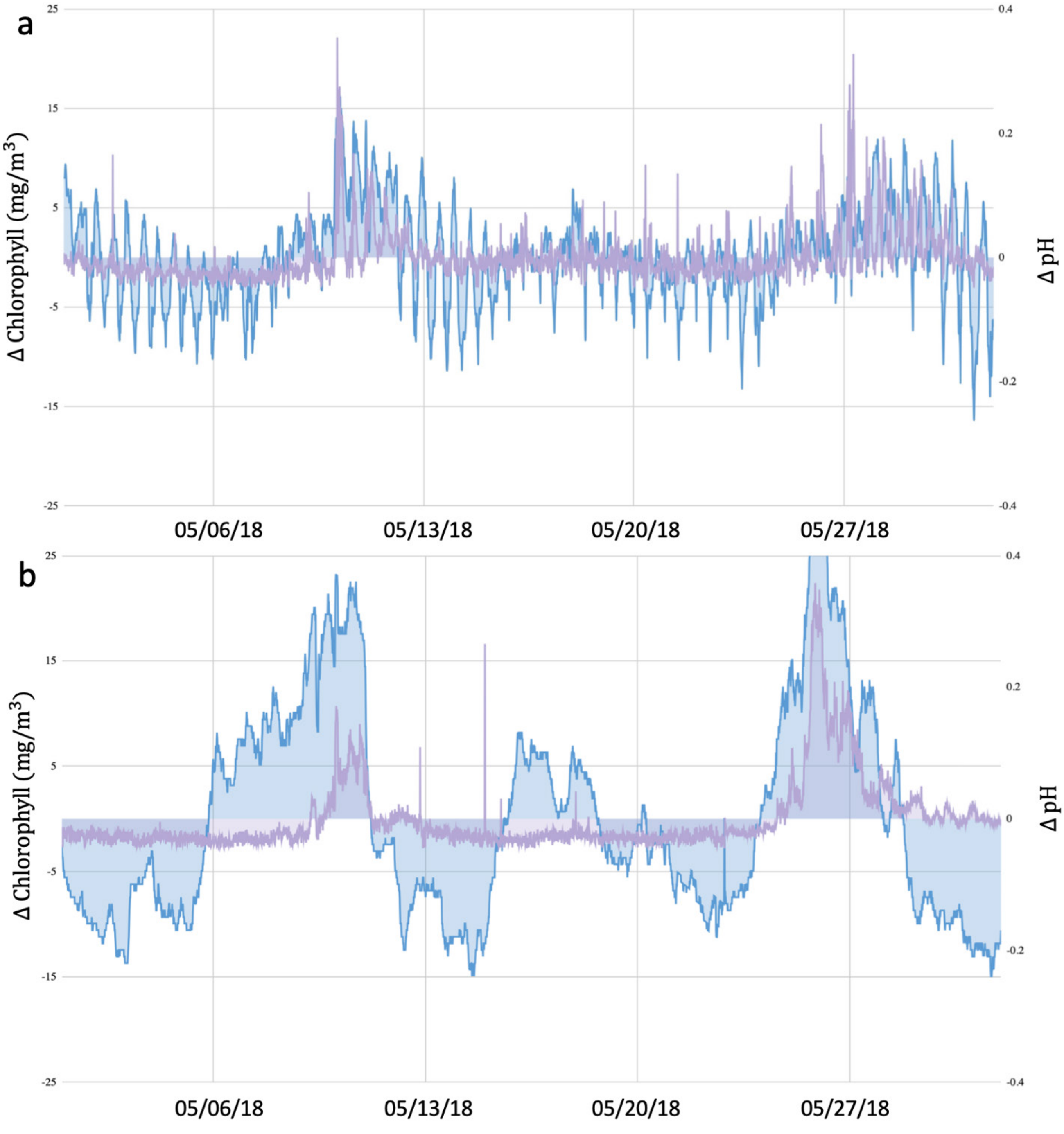
Figure 9.
pH anomalies (blue) and oxygen saturation anomalies (yellow) from the first week of May 2018 at Chevron Dock in Humboldt Bay (a) and at Trinidad Pier (b). Data were obtained from CenCOOS sensors which are continuously deployed at each site collecting pH and DO every 15 minutes. Anomalies were calculated by subtracting the monthly mean from each measurement.



kg. There was an overall increase of ~320 µmol/kg between all stations from the initial day to the final day of the incubation for the mixed bottles (Figure 12). The mixed incubation station with the greatest increase in alkalinity was station NB6 with an increase of 736 µmol/kg and the smallest increase in alkalinity was station NB5 with an increase of 82 µmol/kg.

There was also an increasing alkalinity trend for unmixed incubations, with an average increase of ~34 µmol/kg. The unmixed incubation station with the greatest increase in alkalinity was station NB6, with an increase of 64 µmol/kg, and the smallest increase in alkalinity was station NB5, with an increase of 12 µmol/kg.

Figure 10.
pH anomalies (blue) and chlorophyll anomalies (purple) were collected during the month of May 2018 at Chevron Dock in Humboldt Bay (a) and at Trinidad Pier (b). Data were obtained from CenCOOS sensors which are continuously deployed at each site to collect pH and chlorophyll every 15 minutes. Anomalies were calculated by subtracting the monthly mean from each value.

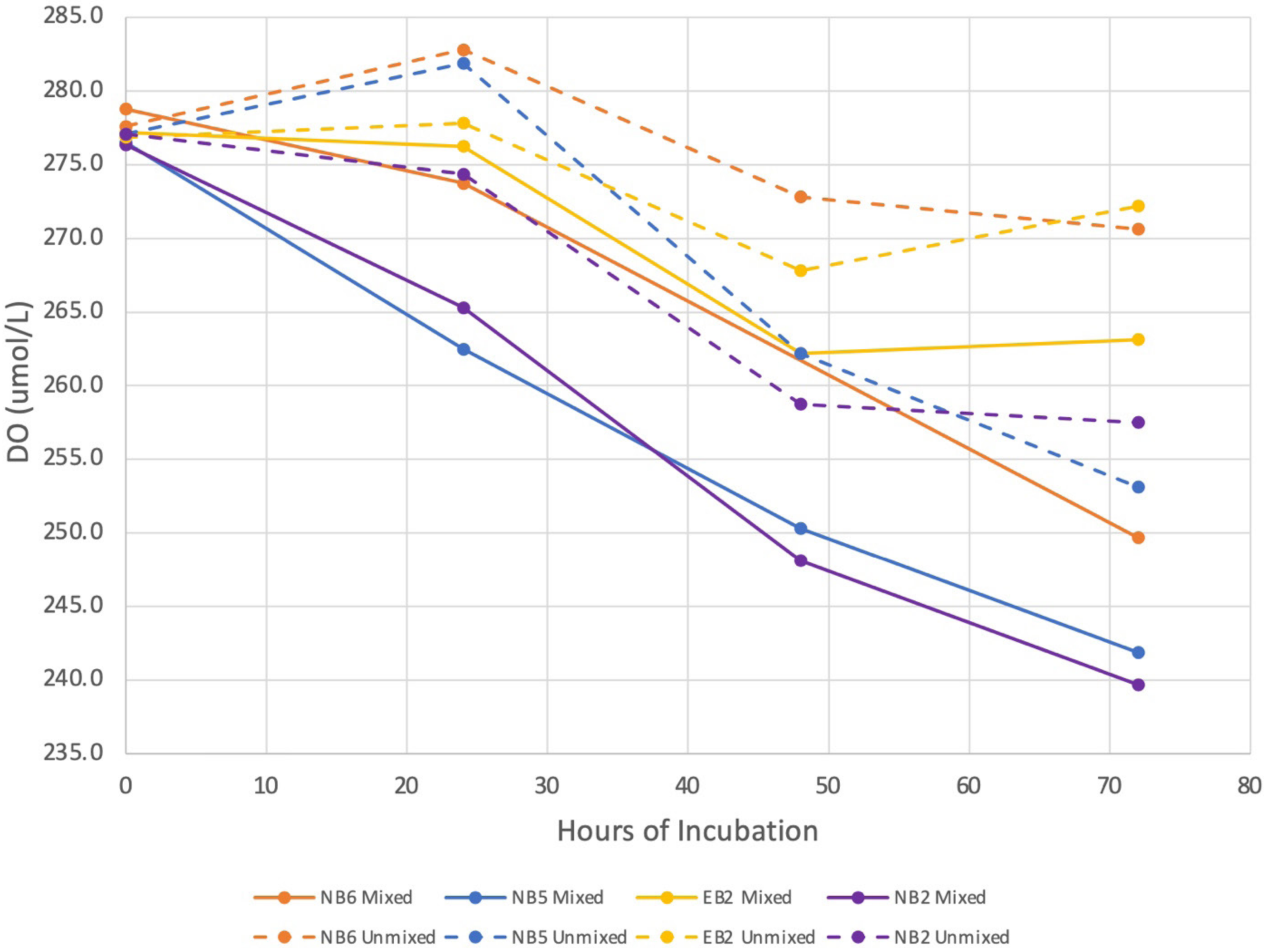


Although there was an increasing alkalinity trend found in both mixed and unmixed incubations, the average increase in alkalinity for the mixed incubations was much greater than for the unmixed incubations. This is likely due to the enhanced dissolution of carbonate ions from the suspended sediments, which increases alkalinity.

Discussion

The main goal of this study was to determine the primary processes that control pH in HB. We hypothesized that the pH in HB is controlled by: 1) the tidal input of coastal waters into the bay; 2) the reduction (increase) of CO_2 due to

Figure 11.
Dissolved oxygen evolution during our three-day incubations. Colors represent stations. Dashed lines represent unmixed samples, and solid lines represent mixed samples mixed by a stir bar during the incubation period. Note the 48-hour BOD bottle for Station NB6 broke, so no data was recorded.



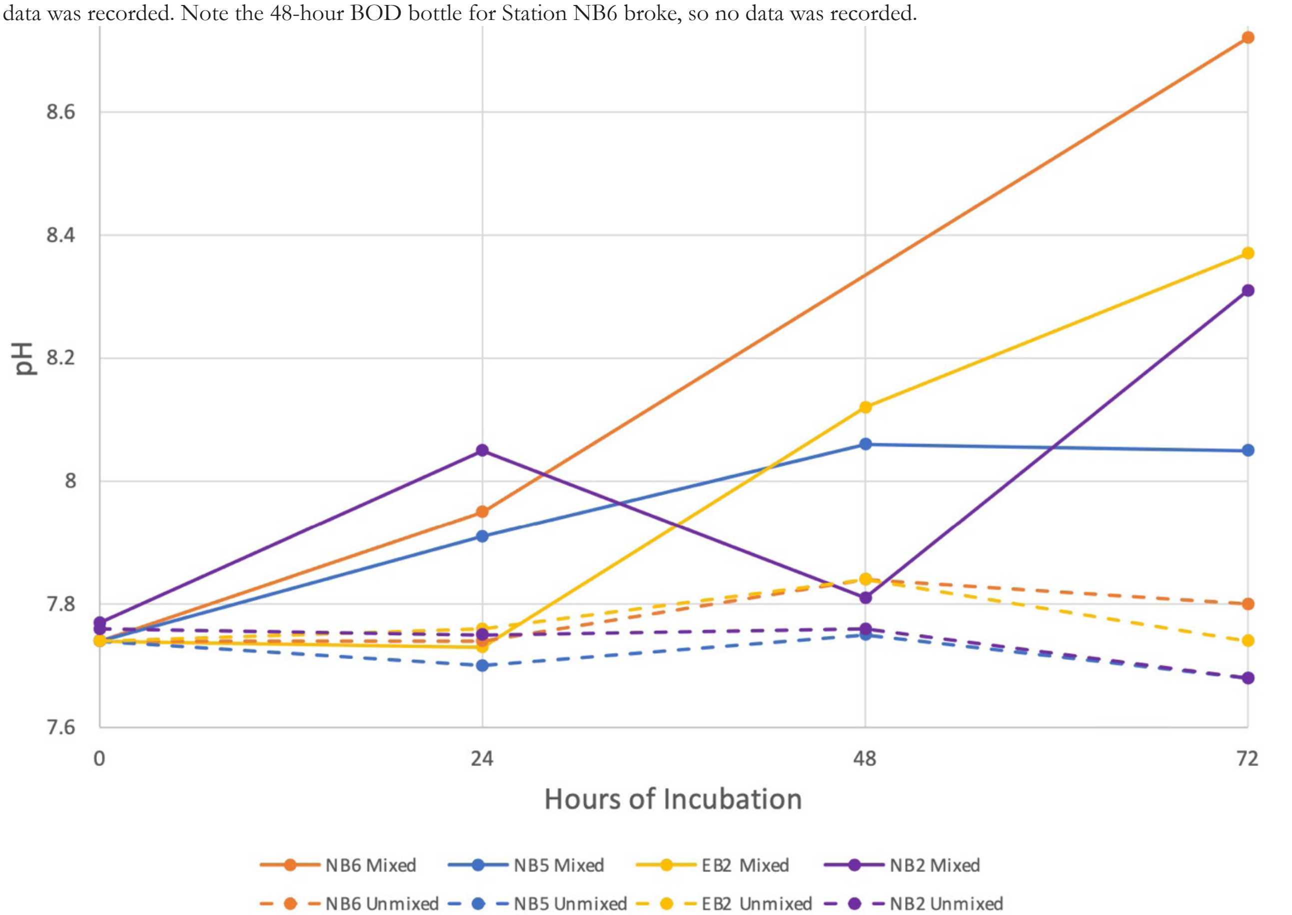
biological productivity (respiration); and 3) the dissolution of carbonate minerals within the sediments due to strong tidal mixing. Based on the results presented here, we conclude that the tides and biological factors each play a major role in controlling HB's pH while the dissolution of carbonates may play a secondary role.

Upwelling and relaxation appear to be the main control for pH in the coastal waters at Trinidad (Figure 5b). Upwelling events are clearly evident when temperature drops several degrees within a few days. This signature is accompanied by an initial drop in DO and pH. Almost immediately after the upwelling subsides, the oxygen saturation rises above 100% due to increased photosynthesis brought about by upwelled nutrients. Chl-a also increases, accompanied by a rapid increase in pH due to the drawdown of CO_2 during photosynthesis.

This coastal upwelling-driven, biological control sets the forcing for the water that enters HB. Water quality parameters within HB, including pH, vary with the tidal cycle. This variability is not consistent, but changes with coastal upwelling. During upwelling events low-pH water enters the bay on the flood tide, and mixes with higher-pH bay waters. The resulting pattern shows depth and pH varying inversely, with lower pH on the flood tide (reflecting the low pH coastal end member), and high pH on the ebb (reflecting the higher pH bay end member) (Figure 7a and the first half of Figure 8). During relaxation periods after upwelling, the trend is reversed. The coastal surface waters undergo a decrease in CO_2 as phytoplankton increase their productivity in response to the upwelled nutrients. This raises the pH and DO relative to the bay waters. This resulting pattern shows depth and pH co-varying with higher pH on the flood and lower pH on the ebb, as can be seen in the second half of figure 8.

The ever-present tidal pattern in pH and other water quality parameters provides strong support for the first hypothesis: HB's pH is strongly controlled by tidal influx. But that can't be the whole story. HB's pH may initially be set

Figure 12.
pH change during the 3-day incubations in artificial seawater. Colors represent stations. Dashed lines represent unmixed samples, and solid lines represent mixed samples mixed by a stir bar during the incubation period. Note the 48-hour BOD bottle for Station NB6 broke, so no data was recorded. Note the 48-hour BOD bottle for Station NB6 broke, so no data was recorded.



by the influx of coastal waters, but the modification of that pH on every ebb tide requires a biological or chemical process within the bay. Otherwise the pH of the bay would vary less with each subsequent tidal cycle until the bay water matched the coastal value and further tidal variation was minimal.

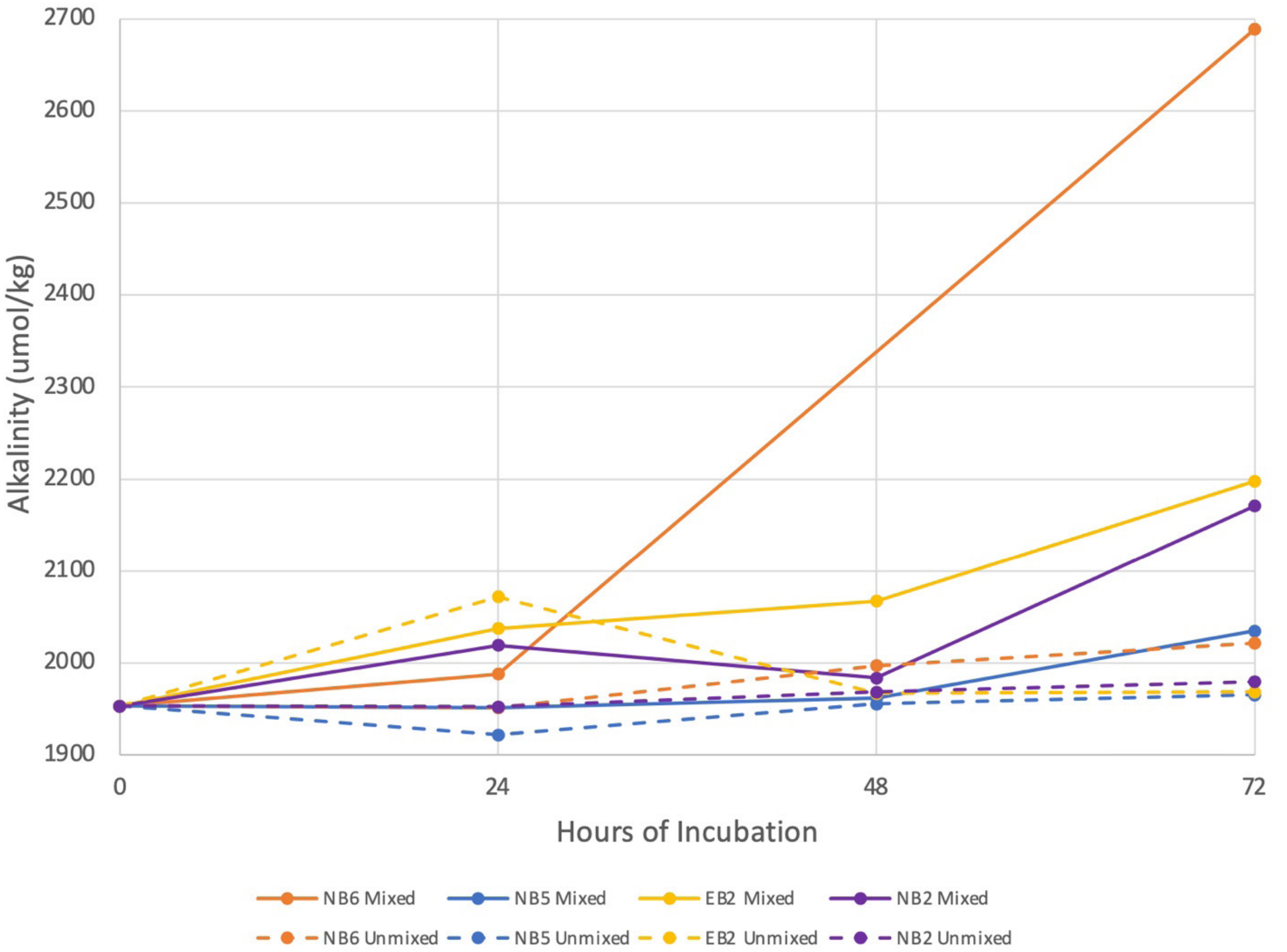
Looking at the biological processes within HB more closely, there is clear support from the CeNCOOS data that primary productivity is raising the pH relative to coastal waters. As at Trinidad, pH and oxygen saturation show strong correlation within the bay. Peaks in pH are accompanied by oxygen saturations greater than 100% (Figure 9). Such high saturations are attainable when excess primary productivity elevates oxygen above the amount expected due to gas exchange alone. Aligning with these peaks in pH and oxygen, chl-a also increases, indicating elevated phytoplankton (Figure 10). The magnitude of chla-a and pH peaks are not always proportional, however, since chl-a is an indicator of phytoplankton but not eelgrass. The data from this study cannot constrain its magnitude, but eelgrass is likely playing a large role in the primary productivity cycle of the bay, which would impact pH and DO without altering chl-a. This could explain some of the mismatch between the timing and magnitude of pH peaks compared to chl-a (Figure 10).

While primary productivity raises pH, respiration counters this effect, lowering pH... When the pH in the bay is less than the pH nearshore, net respiration must be occurring. Net respiration could be caused by a lack of sunlight (night time, overcast, etc.) or nutrient depletion -- both limiting photosynthesis. When the pH nearshore is high, photosynthesis is a primary cause. Excessive photosynthesis raises the nearshore pH, but can also deplete the nutrients in surface waters, limiting the nutrients that get delivered to HB.

In addition to the correlation between pH, DO, and chl-a, the difference between HB and Trinidad pH at similar times provides another indicator that primary productivity and respiration alter pH within the bay. pH is elevated in the bay at the outset of upwelling periods, and is lowered by incoming low-pH coastal waters, but then rises again, showing that photosynthesis effectively raises the pH of the acidic coastal water that enters the bay. Primary productivity provides an

Figure 13.

Mixed and Unmixed Incubation Alkalinity levels. Alkalinity evolution during our three-day incubations. Colors represent stations. Dashed lines represent unmixed samples, and solid lines represent mixed samples mixed by a stir bar during the incubation period. Note the 48-hour BOD bottle for Station NB6 broke, so no data was recorded. Note the 48-hour BOD bottle for Station NB6 broke, so no data was recorded.



important contribution to the pH fluctuation observed within the bay that cannot be attributed to the tidal cycle alone.

Looking more closely at the chemical processes within HB reveals some support that sedimentary carbonate dissolution could act as a pH buffer. Due to the experimental set-up, our incubations indicate the upper limits of the buffering capacity of the sediments. pH and alkalinity varied little in incubations where the sediment was not resuspended, but varied considerably where the sediments were continuously stirred. In these mixed incubations, the pH change over the 3-day experiment (Figure 11) exceeded the observed pH anomalies in HB (Figure 9), and total alkalinity was up to 150 greater than in the unmixed incubations. This indicates that resuspension of the sediments enabled the release of carbonate or silicate ions from the sediment, which reacted with H^+ in the water column to form bicarbonate and silicic acid, respectively. This is the likely reason the mixed incubation pH increased.

Carbonate dissolution alone may be sufficient to drive the observed alkalinity increase. We estimate a maximum of 80 µmol/kg of carbonate available in each incubation (assuming each 0.5 g of sediment added to the 300 g of artificial seawater contained 0.5 weight% $CaCO_3$ in accordance with Bolster et al., 2015). At 2 equivalents of alkalinity per mol carbonate, sedimentary dissolution of all the estimated calcium carbonate would result in a 160 µmol/kg increase in alkalinity. This is on par with the observed results (Figure 11), but complete dissolution over just a 3-day period seems unlikely as carbonate minerals take time to dissolve. Some of the observed alkalinity change could also be due to silicate dissolution, which unfortunately, was not measured during the incubations.

Nonetheless, if carbonate minerals did dissolve, our incubations suggest a substantial impact on the pH of HB that would rival the impact of primary productivity. Given the incubation set-up, we do not believe that is likely for several reasons: 1) the incubation bottles were prepared with artificial seawater that had no Ca^{2+} ion. This created a very low calcium carbonate saturation state despite the realistic levels of CO_3^{2-}. With no calcium ion, dissolution would have taken place more quickly and to a greater extent in the incubation bottles than what would naturally occur in HB; and 2) Sediment resuspension in HB is not constant but occurs periodically for about an hour at a time around max flood and ebb tides. The turbidity observed in the bay fluctuates considerably with the tides and therefore constant resuspension in the bay is unlikely. If we were to confine our incubation results to 4 hours of resuspension per day (i.e. two max flood and two max ebbs); the total pH change of +0.5 would be constrained to +0.03 per day. This is about 20% less than the changes observed due to tidal exchange, primary productivity and respiration.

The increase in pH and alkalinity indicates that carbonate minerals within the sediment likely buffer pH, supporting Hypothesis 2, but the magnitude of that pH change is likely secondary compared to tidal and biological factors.

Conclusion

After analyzing our three hypotheses, we found that there is support that the pH of HB is impacted tidally, and biologically, but to a lesser degree through sedimentary carbonate dissolution. The tidal cycle's effect works similarly to the flushing of a toilet, bringing in coastal water with every flood tide. The pH of the water that enters the bay is primarily determined by the pH of the coastal ocean, which can be higher or lower than the pH seen within the bay depending on the degree of upwelling. Once inside HB, biological processes increase or decrease the pH of the water, depending on the strength of primary productivity relative to respiration. In addition to these major controls, the resuspension of sediment on each max flood and ebb tide likely increases pH due to the buffering effect of carbonate mineral dissolution. The strength of the buffering ability of the carbonate sediments is dependent on turbidity levels and the saturation state of carbonate minerals.

Further study is required to quantitatively ascertain the role of these three processes in controlling pH in HB. Incubations with Ca^{2+} in the artificial seawater, and with a mixing pattern matching the tidal period would better mimic the role of carbonate dissolution in buffering bay pH. Output data from combined tidal and productivity models compared with CenCOOS observations could quantify the primary factors controlling HB's pH. Perhaps more importantly, such models could provide future scenarios for stakeholders and managers to assist in decision making about aquaculture and recreational use of HB.

References

Barnhart, R. A., Boyd, M. J., & Pequegnat, J. E. (1992). *The Ecology of Humboldt Bay, California: An Estuarine Profile*. U.S. Department of the Interior, Fish and Wildlife Service.

Barrett, J. (2004). Sediment Inputs to Humboldt Bay. *Proceedings of the Symposium: Current Perspectives on the Physical and Biological Processes of Humboldt Bay, March 2004*, 35–50.

Bolster, C., Bolt, C., Fisch, M., Halim, K., Jones, N., Mefford, A., Nilsen, C., Peffer, C., Seng, J., Seward, J., Tuttle, N., Ward, C., Borgeld, J., Genger, H., & O'Shea, D. (2015). *NITRATE, NITRITE, AND AMMONIUM CONTENT OF THE WATER, SEDIMENTS, AND BIOMASS IN HUMBOLDT BAY, NORTHERN CALIFORNIA*. https://doi.org/10.13140/RG.2.1.4679.6564

Chavez, F. P., Sevadjian, J., Wahl, C., Friederich, J., & Friederich, G. E. (2018). Measurements of pCO2 and pH from an autonomous surface vehicle in a coastal upwelling system. *Deep Sea Research Part II: Topical Studies in Oceanography*, *151*, 137–146.

Claasen, N. J. (2003). *Modeling wave-current interaction in the vicinity of Humboldt Bay, California* [PhD Thesis]. Humboldt State University.

Doney, S. C., Fabry, V. J., Feely, R. A., & Kleypas, J. A. (2009). Ocean acidification: The other CO2 problem. *Annual Review of Marine Science*, *1*, 169–192.

Fabry, V. J., Seibel, B. A., Feely, R. A., & Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES Journal of Marine Science*, *65*(3), 414–432. https://doi.org/10.1093/icesjms/fsn048

Feely, R. A., Alin, S. R., Newton, J., Sabine, C. L., Warner, M., Devol, A., Krembs, C., & Maloy, C. (2010). The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary. *Estuarine, Coastal and Shelf Science*, *88*(4), 442–449. https://doi.org/10.1016/j.ecss.2010.05.004

Feely, R. A., Doney, S. C., & Cooley, S. R. (2009). Ocean acidification: Present conditions and future changes in a high-CO_2 world. *Oceanography*, *22*(4), 36–47.

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

Fodrie, F. J., Rodriguez, A. B., Gittman, R. K., Grabowski, J. H., Lindquist, Niels. L., Peterson, C. H., Piehler, M. F., & Ridge, J. T. (2017). Oyster reefs as carbon sources and sinks. *Proceedings of the Royal Society B: Biological Sciences*, *284*(1859), 20170891. https://doi.org/10.1098/rspb.2017.0891

Gattuso, J.-P., & Hansson, L. (2011). *Ocean Acidification*. OUP Oxford.

Gilkerson, W. A., & Merkel, K. W. (2017). *Humboldt Bay Eelgrass Comprehensive Management Plan. Prepared for Humboldt Bay Harbor, Recreation, And Conservation District.* Merkel & Associates, Inc.

Lim, Y.-K., Dang, X., & Thiyagarajan, V. (2021). Transgenerational responses to seawater pH in the edible oyster, with implications for the mariculture of the species under future ocean acidification. *The Science of the Total Environment*, *782*, 146704. https://doi.org/10.1016/j.scitotenv.2021.146704

Monroe, G. M., Thompson, S. J., Swartzell, P. G., Browning, B. M., Speth, J. W., & Arnett, G. R. (1973). *The natural resources of Humboldt Bay* (Issue 6). California Department of Fish and Game. http://hdl.handle.net/1834/18463

Moore, J. E., Colwell, M. A., Mathis, R. L., & Black, J. M. (2004). Staging of Pacific flyway brant in relation to eelgrass abundance and site isolation, with special consideration of Humboldt Bay, California. *Biological Conservation*, *115*(3), 475–486. https://doi.org/10.1016/S0006-3207(03)00164-2

Rassmann, J., Lansard, B., Gazeau, F., Guidi-Guilvard, L., Pozzato, L., Alliouane, S., Grenz, C., & Rabouille, C. (2018). Impact of ocean acidification on the biogeochemistry and meiofaunal assemblage of carbonate-rich sediments: Results from core incubations (Bay of Villefranche, NW Mediterranean Sea). *Marine Chemistry*, *203*, 102–119. https://doi.org/10.1016/j.marchem.2018.05.006

Ricart, A. M., Ward, M., Hill, T. M., Sanford, E., Kroeker, K. J., Takeshita, Y., Merolla, S., Shukla, P., Ninokawa, A. T., Elsmore, K., & Gaylord, B. (2021). Coast-wide evidence of low pH amelioration by seagrass ecosystems. *Global Change Biology*, *27*(11), 2580–2591. https://doi.org/10.1111/gcb.15594

Ries, J. B. (2011). A physicochemical framework for interpreting the biological calcification response to CO2-induced ocean acidification. *Geochimica et Cosmochimica Acta*, *75*(14), 4053–4064. https://doi.org/10.1016/j.gca.2011.04.025

Schlosser, S., & Eicher, A. (2012). *Humboldt Bay and Eel River Estuary Benthic Habitat Project* (T-075). California Sea Grant. https://caseagrant.ucsd.edu/our-work/e-documents/humboldt-bay-and-eel-river-estuary-benthic-habitat-project

Shen, C., Testa, J. M., Li, M., Cai, W.-J., Waldbusser, G. G., Ni, W., Kemp, W. M., Cornwell, J., Chen, B., Brodeur, J., & Su, J. (2019). Controls on Carbonate System Dynamics in a Coastal Plain Estuary: A Modeling Study. *Journal of Geophysical Research (Biogeosciences)*, *124*, 61–78. https://doi.org/10.1029/2018JG004802

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., 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

Sullivan, R. M., Laird, A., Powell, B., & Anderson, J. K. (2022). Sea level rise vulnerability assessment for State wildlife areas surrounding Humboldt Bay, northern California. *California Fish and Wildlife Journal*, *108*(4). https://doi.org/10.51492/cfwj.108.24

Werblow, S., & Cobo y Gonzales, J. M. (2020). *Exploring Eelgrass | Capturing CO2 with Shallow-Water Beds*. https://www.ysi.com/ysi-blog/water-blogged-blog/2020/07/exploring-eelgrass-capturing-co2-with-shallow-water-beds