

Spatial and Temporal pH Variability in a California Estuary During the Winter Wet Season

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By:
Garrett Schmid (Marine Science Department)

Advised by:
Dr. Emily Bockmon (Chemistry Department)
Dr. Ryan Walter (Physics Department)

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1. INTRODUCTION

Anthropogenic stressors such as increased atmospheric carbon dioxide (CO₂) are impacting carbonate chemistry in the global ocean by decreasing the pH, a process known as ocean acidification. (Doney et al., 2009; Feely et al., 2009; Orr et al., 2005). The direct impact of anthropogenic CO₂ emissions on the nearshore coastal ocean and estuarine environments is largely uncertain (Duarte et al., 2013). In particular, estuaries are highly dynamic and productive biogeochemical systems (Bauer et al. 2013; Wang et al. 2016); however, information regarding the spatial and temporal variations of carbonate chemistry within these environments is limited (Cai et al. 2011; Hofmann et al. 2011; Waldbusser et al. 2011).

The variability of the carbonate chemistry in estuaries is driven by both physical and biological processes (Flecha et al., 2015; Joesoef et al., 2017). Physical processes are largely governed by the interplay between freshwater discharge and tidal forcing (and mixing). Spatially, the back of an estuary (i.e, the head) is typically more strongly influenced by riverine input while the front of an estuary (i.e., the mouth) is regulated by tidal forcing and oceanic inputs. Biological processes influence the carbonate chemistry predominantly via primary production, microbial respiration (Waldbusser & Salisbury 2014), precipitation (calcification) and dissolution of calcium carbonate (Wolf-Gladrow et al., 2007). Primary production, from autotrophic organisms such as phytoplankton, macroalgae, and eelgrass, can increase seawater pH and dissolved oxygen (DO) of the surrounding water through the consumption of CO₂ and the release of oxygen (O₂) (Middelboe and Hansen 2007). Marine respiration decreases pH and DO through the consumption of O₂ and the release of CO₂.

Seasonally, low-inflow estuaries (LIEs) are a class of estuaries typically found in Mediterranean climates whereby freshwater input is minimal during the summer “dry” season and increases during the winter “wet” season (Largier, 2010; Walter et al., 2018). These seasonally LIEs are relatively understudied compared to classically defined estuaries with freshwater input throughout the year (Largier, 2010; Walter et al., 2018). The summertime is characterized by minimal freshwater input and high evaporation which can create a hypersaline environment if residence times are long (Largier, 2010). During periods of low river discharge, the water movement in the estuary is largely driven by the tides. Additionally, increased solar intensity during the summer can promote net autotrophy, leading to increased pH in the estuary (Brodeur et al., 2019; Middelboe et al., 2006). Conversely, the winter “wet” season involves periods of increased precipitation, followed by freshwater discharge. During these intermittent events, variable changes to the estuary (i.e. nutrient/sediment input, mixing, biological response), resulting from riverine input, may alter the carbonate chemistry.

Estuaries are highly dynamic and provide important functions to the environment (i.e. sequesters carbon, supports biodiversity) and changes to carbonate chemistry can impact these biological processes (Doney et al., 2009). Thus, it is essential to understand the factors influencing carbonate chemistry variability in estuaries. Recent work has illustrated the range of time scales at which carbonate chemistry varies in coastal systems, and therefore, continuous, high-frequency sampling is necessary to observe the variations in a dynamic estuarine environment (Waldbusser & Salisbury, 2014; Hoffmann et al., 2011). In addition, Hoffmann et al., (2011) have shown efficacy using autonomous pH sensors to sample in coastal regions. Here, I present the first continuous, high-frequency pH data during a winter ‘wet’ period in a LIE located on the Central California Coast (Morro Bay Estuary). The overall objective of this study is to understand the primary drivers of pH variability (both spatially and temporally).

2. METHODS

2.1 Site Overview

Morro Bay, located on the Central Coast of California along the California Current, is a small (6km long) tidally-forced seasonally LIE (Walter et al. 2018). During the short and intermittent wet season, a positive estuary arises, denoted by freshwater input at the estuary head. The dry season (Apr.- Nov.) has high rates of evaporation (along with low freshwater input) which can cause the estuary to be hypersaline (Walter et al. 2018). During the winter season, there are two main sources of freshwater input (Chorro Creek and Los Osos Creek) from the adjacent watershed (~2300 acres), with the majority of the freshwater input from Chorro Creek (MBNEP, 2015). Morro Bay's benthic zone was once dominated by eelgrass (*Zostera marina*), but since 2007, more than 90% of the seagrass has been lost, without a clear culprit. The Morro Bay National Estuary Program (MBNEP) is currently performing restoration efforts and has seen success with select methods (MBNEP, 2018).

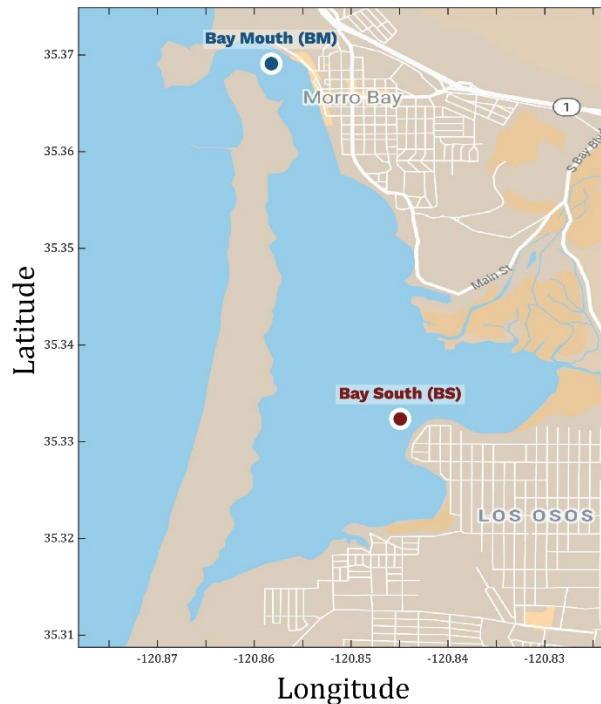


Figure 1 The Morro Bay estuary site. The blue and red dots represent the BM and BS locations, respectively.

2.2 Data Sources

Two stations in Morro Bay were equipped with autonomous sensor packages to measure chemical and physical parameters from 10 January to 15 February 2019. The Bay Mouth station (BM) was located near the estuary inlet (35°22'14.9"N 120°51'31.3"W; Fig. 1) and the Bay South station (BS) was located in the back of the bay (35°20'01.6"N 120°50'50.2"W; Fig. 1). The average water depth at BM and BS was 10.2 m and 2.27 m, respectively. At each site, both a MiniFET pH sensor and a Sea-Bird Electronics 37-SMP conductivity-temperature-depth (CTD) sensor were deployed on a mooring. The MiniFET pH sensor uses

an ISFET (ion-sensitive field-effect transistor) sensing element without a reference electrode to collect pH data at a 5-minute sampling interval and was provided by Yui Takeshita at MBARI. BM and BS MiniFETs were attached at 3.6 m and 0.6 m above the seabed, respectively. The CTDs were approximately co-located near each MiniFET and located 2 m above the bed at BM and 0.65 m above the bed at BS. BM included a DO sensor which was attached to the CTD and limited the sampling period at the site (BM: 2.5 min; BS: 15 sec). Last, river discharge data from Chorro Creek was calculated using stage height data collected from the San Luis Obispo County Canet Station (https://wr.slocountywater.org/site.php?site_id=41&site=093f8e0b-dfde-4a45-b291-174ce07ead12) and converted to discharge data using a stage-discharge relationship (MBNEP 2015). All times referenced are in local time (Pacific Standard Time).

2.3 Calibration Calculation

To calibrate the Minifet sensor, discrete water samples were collected near the sensor deployment sites. The first set of samples were collected on 6 February 2019 at 11:35am and 1:10pm at BM and BS, respectively. The samples were collected using a handheld Niskin bottle via SCUBA next to the Minifet sensors. The divers also lightly scrubbed the sensors' external copper biofouling guard. All discrete samples were poisoned with HgCl_2 and stored in a cool dark room until analysis using an automated spectrophotometric pH instrument, calibrated to a certified reference material (CRM), following the best practices as described in Dickson et al., 2007. The pH at in-situ temperature was calculated using CO2SYS (Lewis and Wallace 1998; Pelletier et al. 2007), using the CTD temperature measurements. The sensor calibration was performed by finding the pH offset between the discrete sample and MiniFET sensor at the time the sample was collected. These additive offset quantities (BM and BS) were applied to the entire MiniFET time series at each location.

2.4 Data Processing

The data were imported into MATLAB 2019a for processing and plot generation. To observe the low frequency variations and to remove the tidal effects, a 36 hr low-pass filter (i.e., hereafter referred to as a 'subtidally filtered') was applied in some analyses (Fig. 2). To understand how tides affect variability in other parameters (e.g., pH, temperature, salinity), and to standardize values between locations, I calculated tidal height anomalies by removing the average depth over the entire experiment at each respective site from the time series of depth derived from the CTD pressure sensor.

On 7 February, the BM MiniFET sensor malfunctioned. While the cause of the failure is unknown, after this date, the pH data were characterized by high frequency and high magnitude fluctuations. I calculated temporal derivatives between each sample value to verify that the increased rate of change did not match preceding data at BM or any data at BS. Thus, the BM data shown below are before 7 February at 2:00 pm (Fig. 2) and scatterplots that utilize both BM and BS (Fig. 3 & 7) only compare the data at these two sites until this time.

3. RESULTS

3.1 Entire Dataset:

3.1.1 Spatial comparisons

Throughout the 34-day sample period, the pH varied between locations and across time. The average pH at BM [7.86] was higher than the average at BS [7.82] and the subtidally filtered pH (Fig. 2c) at BM was higher than BS during the entirety of the dataset. The variance in pH (Jan 11 to Feb 7) was comparable between sites [BM 0.035 SD and BS 0.042 SD]. The BM site had a higher average salinity [BM: 32.86 and BS: 31.38] and a smaller range compared to BS. There were two large periods of freshwater discharge captured throughout the study (Fig. 2a) which caused subsequent decreases in the estuary's salinity (Fig. 2e). Additionally, there were two notable periods when the temperature in the BS location exceeded BM, as identified by the subtidally filtered temperature record (Fig. 2d). The first warm period (17 to 21 Jan) at BS occurred after the first discharge event while the second warm period (29 Jan to 1 Feb) occurred just before the second discharge event. Two spring-neap tides cycles (Fig. 2b) were captured during the study and in general, the daily variations in pH, temperature, salinity, and DO matched the temporal variations in tides. Spatially, there were larger standard deviations at BS in both temperature [BM 0.53 SD and BS 0.82 SD] and salinity [BM 1.14 SD and BS 2.09 SD] (Fig. 2c, d, and e).

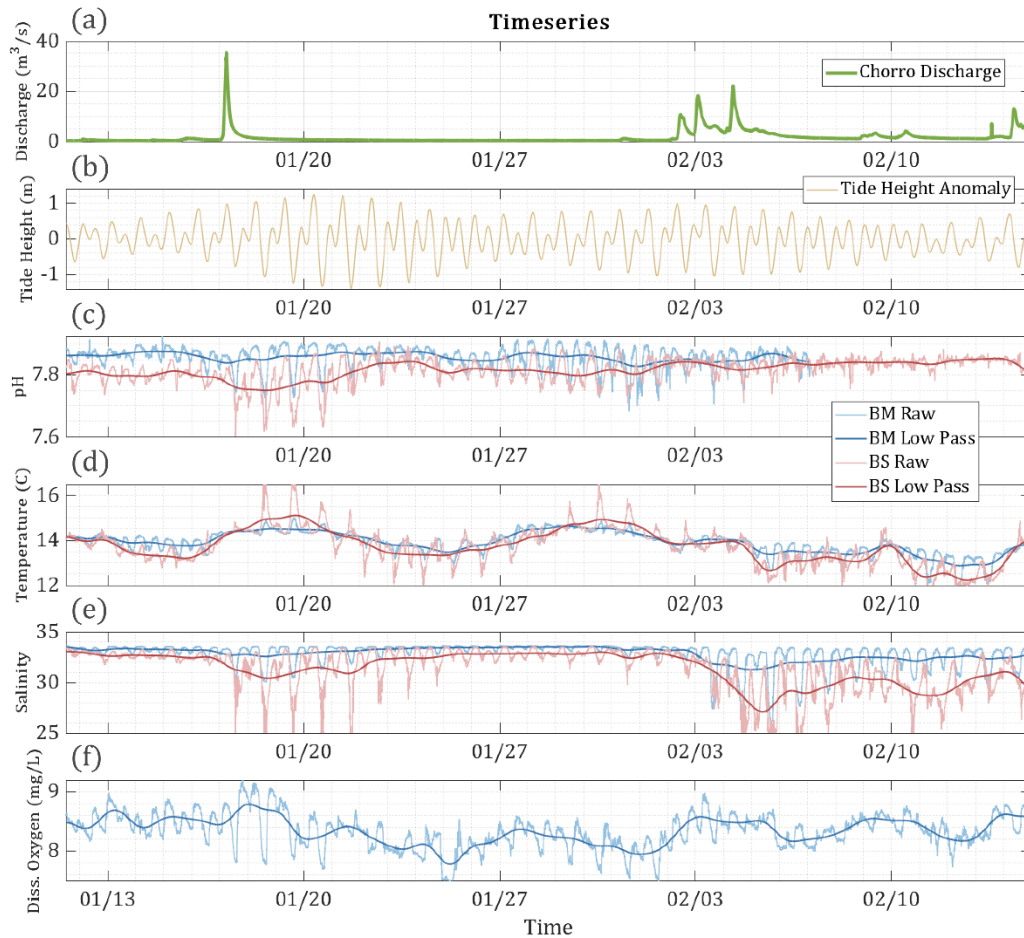


Figure 2 Time series plots of the entire sampling period including (a) discharge from Chorro Creek, (b) tide height from BM CTD water depth anomaly, (c) pH, (d) temperature, (e) salinity, and (f) dissolved oxygen. The blue and red lines correspond to the BM and BS, respectively. The darker and thicker lines (red and blue) represent the subtidally filtered time series (i.e., 36 hr low-pass filtered).

3.1.2 Tidal Influence

The pH in Morro Bay was largely driven by tidal variability at both sites. Higher tides were generally correlated with higher pH values at both BM and BS (Fig. 3a and e). However, during low tides, a wide range in pH was observed, particularly at the BS site. The increased variability during low tides was also observed in temperature and salinity throughout the study (Fig. 3b, f, c, and g). DO ranges were comparable between high and low tides but increased tidal height was generally correlated with higher DO values.

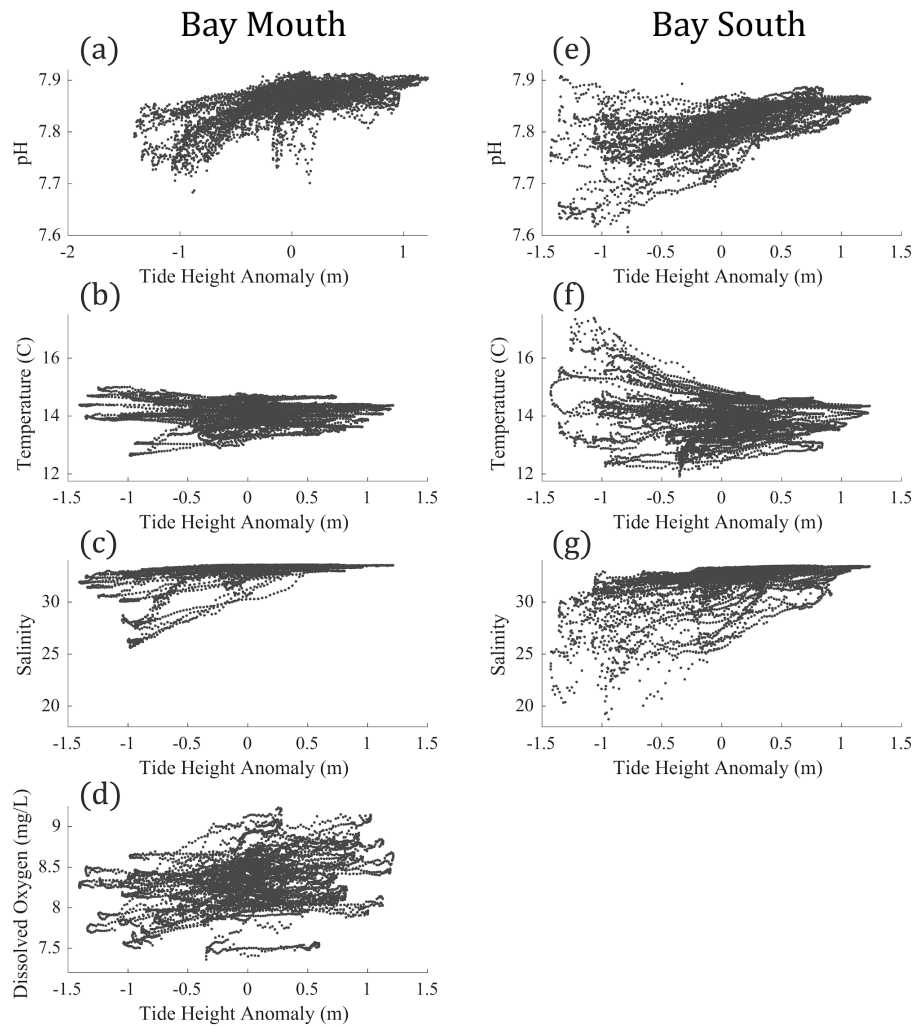


Figure 3 Scatter plots categorized spatially with BM on the left and BS on the right. At each location, (a & e) pH, (b & f) temperature, (c & g) salinity, and (d) dissolved oxygen (only BM), is plotted with respect to the tide. The plots include data until 7 Feb 2:00 am (when the BM pH sensor failed).

3.2 Temporal Events:

3.2.1 Discharge Events

During this study, there were two defined precipitation events, which led to an influx of freshwater discharge into the estuary via Chorro Creek (Fig. 2a). The first event (17 Jan) was characterized by a large magnitude, but short duration, discharge with a cumulative volume of 1573.8 m³. The second event, which began on 3 Feb, was characterized by a weaker magnitude, but a longer duration (~2.5 days) discharge with a cumulative volume of 2889.2 m³. After each discharge event, there was a corresponding drop in salinity (Fig. 2e).

3.2.2 Freshwater influence

To characterize the influence of freshwater, we identified distinct periods based on the subtidally filtered salinity at BS, which is adjacent to Chorro Creek. We chose a cutoff salinity of 32.3, which delineates various sections of the dataset (Fig. 4). During the two periods where the salinity dropped below 32.3, the data were identified as the 'Freshwater Influence' (FW1 & FW2) and above the threshold, classified as the 'Winter Background State' (WBG). FW1 spans from 16 Jan 10:50 pm to 22 Jan 5:30 pm and the FW2 spans from 2 Feb 3:30 pm to 7 Feb 2:00 pm (Fig. 4). The FW1 period included the peak discharge rate (Fig. 5a), meaning the subtidally filtered salinity fell below 32.3 before the first large freshwater input event, likely due to precipitation before 2 Feb. FW2 captured two of the three sequential discharge peaks above 10 m³/s (Fig. 5f).

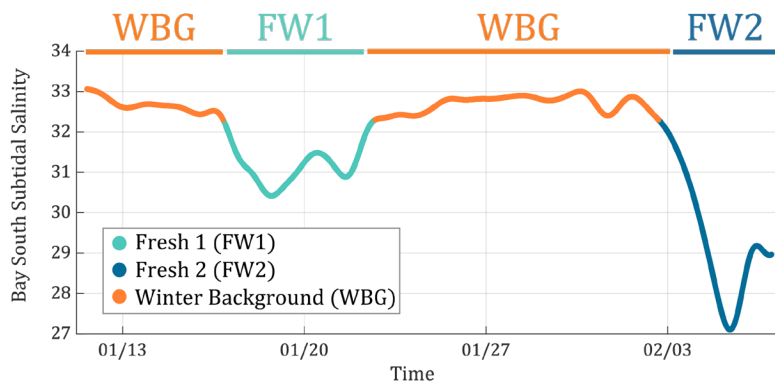


Figure 4 The Bay South subtidally filtered salinity data divided into 3 sections based on a 32.3 salinity cutoff value. The winter background state (WBG) is identified as the period of time above the threshold value and the two Freshwater Influence sections (FW1 and FW2) are characterized as below the threshold salinity value.

During the two freshwater influence sections, the pH responded differently (Fig. 5b and g). FW1 was characterized with both larger pH fluctuations [BM: 0.044 SD & BS: 0.062 SD] and increased spatial variability (0.08 ΔpH). During FW2, the pH experienced smaller site variability [BM: 0.030 SD & BS: 0.023 SD] and spatial variability (0.02 ΔpH). While the magnitude of variance was different, the pH had the same directional relationship with the tide during both freshwater sections (Fig. 5b and g).

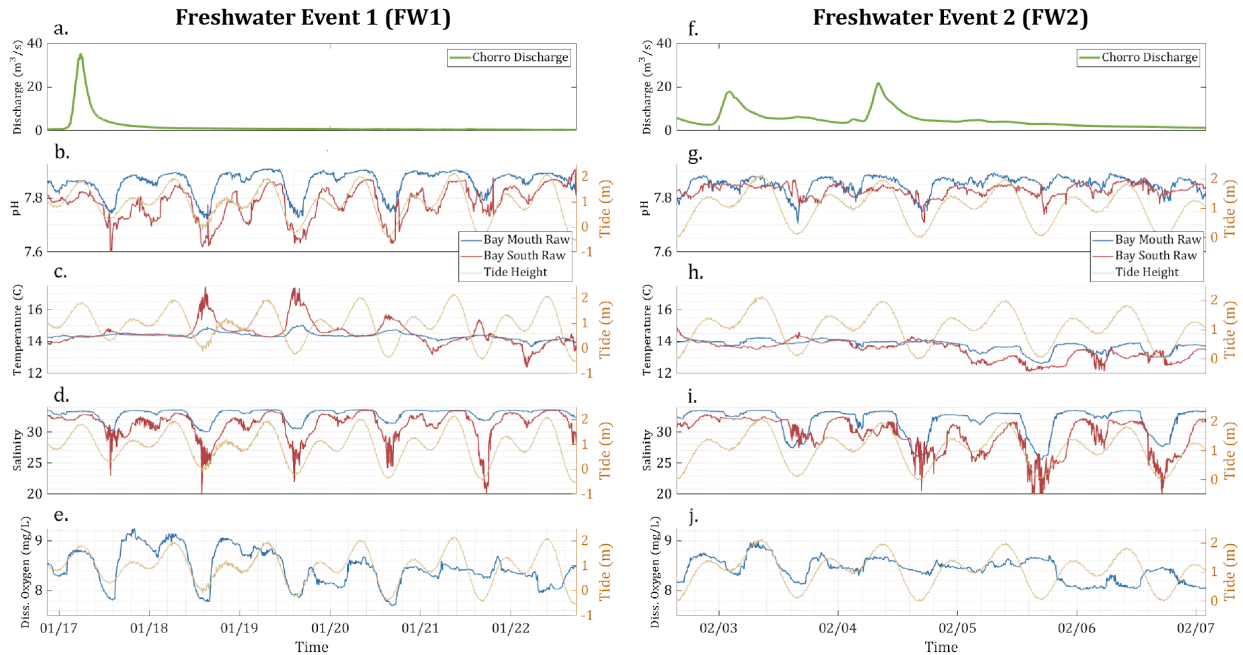


Figure 5 Time series plots of the two freshwater influence events (FW1 and FW2) including discharge from Chorro Creek, pH from the two Minifet sensors, and temperature, salinity, and dissolved oxygen from the two CTD stations in the Morro Bay Estuary. The blue line represents the Bay Mouth (BM) site and the red line represents the Bay South (BS) site. Tide height (yellow) is overlaid on the subplots to point out the clear impact driven by tide.

Temperature, salinity, and DO also experienced different responses between the two freshwater events. FW1 was distinguished by higher average temperatures [BM: 14.33°C & BS: 14.38°C] compared to FW2 [BM: 13.70°C & BS: 13.29°C] (Fig. 5c) and BS had larger temperature fluctuations during FW1 [0.70 SD] than FW2 [0.59 SD]. Unlike pH and temperature, salinity variations were smaller during FW1 [BM: 0.89 SD & BS: 2.17 SD] relative to FW2 [BM: 2.12 SD & BS: 2.86 SD]. DO ranges were larger in FW1 [1.561 mg/L] compared to FW2 [0.966 mg/L] but had comparable average values (Fig. 5e and j).

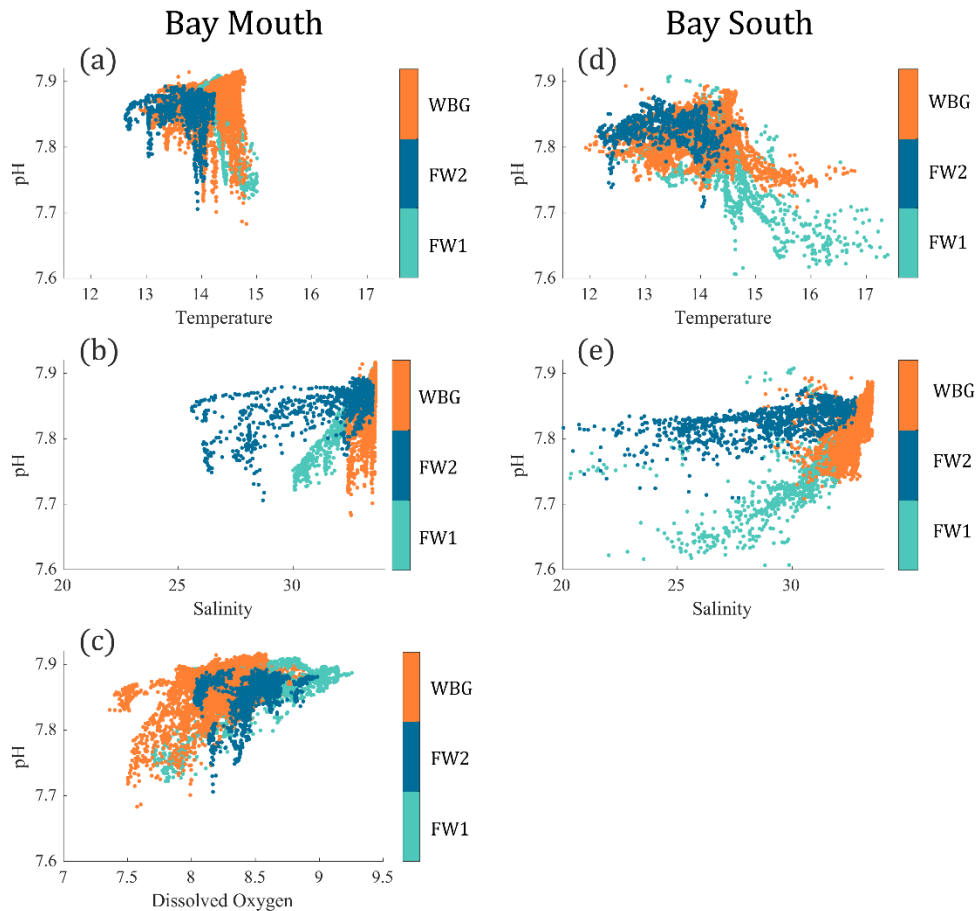


Figure 6 Scatter plots categorized spatially with the BM site on the left and the BS site on the right. At each location, the correlation between temperature, salinity, and dissolved oxygen (only BM) with pH is displayed. The color bar indicates the three sections which correspond to the grouping identified by figure 4. FW1 (light green), FW2 (turquoise), and WBG (orange) are displayed on each subplot. Each section has a different amount of data points, with the WBG state including the largest quantity.

Relationships between pH and each of the other measured parameters varied drastically during the different events and across sites (Fig 7). The BM pH range was comparable between FW1 and FW2 and largest during WBG [FW1: 0.19, FW2: 0.19, WBG: 0.29] (Fig. 6a). BS observed the largest changes in pH during FW1 [FW1: 0.31, FW2: 0.19, WBG: 0.19] (Fig. 6b). Generally, temperature and pH had a negative relationship (Fig. 6a and d). FW1 and FW2 experienced distinct temperature-pH relationships between sites. Specifically, BM had comparable ranges and strength across each section (Fig. 6a) while BS had notably low pH and higher temperatures during FW1 (Fig. 6d). The salinity-pH relationship was positive across time and space (Fig. 6b and e). Further, FW1 was distinguished by larger changes in pH per change in salinity (ie. greater positive slope) compared to FW2 in both sites (Fig. 6b and e). The positive DO-pH relationships were similar across each section, although small subtleties, such as larger DO averages and smaller DO ranges during the FW events were noticeable differences (Fig. 6c). The relationships at each time period were distinct, indicating the discharge events impacted the estuary's water characteristics differently each time period.

4. DISCUSSION

4.1 Seasonality

In this study, we characterized the spatiotemporal pH variability in the Morro Bay Estuary during a 34-day period in the winter wet season. The wet season on the Central Coast of California typically lasts from December to March (and sometimes November to April). Thus, the results and range of pH values observed [BM: 7.68-7.98, BS: 7.59-7.91] may only be applicable during these winter months. During the dry season (typically April to November), results likely differ due to a change in source waters (i.e., little freshwater inputs) as well as different circulation dynamics and residence times throughout the bay. For example, the residence time in back portions of Morro Bay was previously found to be up to 30 days during the summer dry season (Walter et al., 2018). However, during periods of freshwater input, where estuarine (gravitational) circulation develops, it is expected that the residence time will be shorter, minimizing spatial gradients throughout the estuary (Defne and Ganju 2015). In our study, the pH at the estuary head was persistently lower (Fig. 2c), and the freshwater discharge was more acidic than the ocean source waters.

The two discharge events that were captured (Fig. 2a), have different average pH values and distinct relationships with other oceanographic parameters. This research highlights the need to further understand how freshwater inflows affect carbonate chemistry variability in estuarine systems (Yao and Hu 2017; Crosswell et al., 2014). Additionally, past research on the hydrodynamics of Morro Bay has been limited to low-inflow periods (Walter et al., 2018).

4.2 Tidal Influence

Previous studies in estuarine environments have shown that pH is driven by a combination of both physical and biological processes (Flecha et al., 2015; Joesoef et al., 2017). For biologically driven systems, there is typically a strong pH-DO relationship, indicating a metabolically-driven system (Lowe et al., 2019; Challener et al., 2015). In this study, although DO data were only available at BM, DO variability did not display the same tidal patterns observed with pH, temperature, and salinity (Fig. 3). Furthermore, pH and DO were not tightly correlated (Fig. 6c), as in the metabolically driven systems. Given this, physical factors (i.e. tidal forcing and freshwater discharge) likely play a larger role than biology in driving pH variability at BM (where DO data were available). We note that additional DO measurements in the back bay could identify spatial differences in biological processes. Additionally, there are relatively few studies that have assessed pH-DO relationship as a means for distinguishing physics- vs biology-controlled pH variability in estuaries, thus requiring further study.

Net autotrophic estuaries usually experience a higher pH during the day than during the night (Middelboe and Hansen 2007; Cyronak et al., 2018; Paulsen et al., 2018). In this study, the largest pH values at both sites were typically found in the morning, which corresponded to the largest tidal heights observed. Consequently, the absence of a defined biological signal may suggest that Morro Bay is not a net autotrophic ecosystem and that physical processes drive more pH variability during the wet period. While the Morro Bay estuary is not currently dominated by seagrasses, as it was previously (cf. Walter et al. 2018), if recovery efforts continue, the increase in seagrasses (or other macroalgae) could increase the

biological influence on pH variability (Challener et al. 2015). Moreover, there may be strong seasonal differences in the biological influence on pH variability associated with seasonal differences in aquatic vegetation. We highlight the need to collect nutrient and chlorophyll-a concentrations concurrent with carbonate measurements in Morro Bay to provide insight into the estuary's biological influence, particularly in this period of eelgrass restoration.

During this study, pH showed considerable variability across different low tides events near the estuary head (Fig 3e). Larger pH variability at shallow depths has been observed in other estuarine systems such as Mission Bay, Hood Canal, Puget Sound, and Roskilde Fjord (Cyronak et al., 2018; Lowe et al., 2019, Middelboe and Hansen 2007). In Morro Bay, Walter et al. (2018) observed larger variability in temperature and salinity toward the estuary head compared to the mouth during a summer study. The shallow, low tide variations in Morro Bay (Fig 3b, d, & e) is likely due to the smaller volumes of water and higher residence times in the back bay, which is subject to more biological influences; processes at the sediment-water interface (Middelboe and Hansen 2007); and physical processes such as radiative heating, evaporation, limited tidal mixing, and increased influence from land-based runoff (Walter et al. 2018). The low tide variations provide the best indication that biology may have a small but direct influence on the pH during the wet season.

4.3 Freshwater Influence

Previous studies have emphasized that the variability of nutrient input and sediment load from discharge events is dependent on the magnitude and frequency of inflow (Miller et al., 2008; Roy et al., 2013; Scharler and Baird 2005). The two discharge events captured in the study displayed different responses in the estuary, despite being in a similar phase of the spring-neap tidal cycle. The discharge event on 17 January (Fig 5a) exceeded 35 m³/s and was the first large freshwater input into the estuary (above 15 m³/s) during this wet season. The second discharge event was smaller in magnitude (max: 22 m³/s) and longer in duration (3 days compared to 1 day). In FW1, a decline in the subtidally filtered pH was seen at both sites (Fig 2c), while FW2 showed no apparent differences in the subtidally filtered pH. It is likely that the carbonate chemistry of the source waters (i.e., freshwater discharge) was different during each event, and this should be accounted for in future studies.

Broadly, the frequency and magnitude of the river discharge into the estuary likely impacts the pH response. Currently, there are limited studies that have focused on the carbonate chemistry response to episodic freshwater inflow events, and thus, a larger set of events is needed to better understand their influence on pH variability.

5. CONCLUSION

The data presented provide insight into the physical and chemical variability of a LIE during the winter wet season. In this study, Morro Bay's spatiotemporal variability in pH was largely attributed to tidal forcing with intermittent influence from freshwater discharge events. Even within Morro Bay's relatively short length, we still observed spatial gradients in pH and other parameters. This study emphasizes the need to sample and assess the estuarine response and chemical variability over different seasons and additional discharge events of varying magnitude and duration.

Estuaries are subject to human modification through the alteration of source waters (i.e. fertilizers, sewage) and it is important to understand the anthropogenic influence relative to the natural variability. While it is difficult to identify background variability amid climate change and shorter-term impacts (e.g., loss of eelgrass), longer time series studies will better discern the spatiotemporal changes in dynamic environments and potentially the role that humans play in modifying this variability. This study adds to a growing body of literature suggesting the need to expand long-term carbonate chemistry monitoring in estuaries and coastal environments globally.

Acknowledgments:

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