Biological processes drive diel pH signals near shore

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Summer 2014

Keywords: biogeochemistry, pH, signal, ocean acidification, anthropogenic, near shore

ABSTRACT

Ocean acidification, driven by rapidly-escalating anthropogenic CO_2 emissions, is of particular concern near shore, where calcifying organisms are concentrated. How pH, photosynthesis, and respiration interact in this environment is not precisely known. This paper demonstrates the effect of photosynthesis and respiration on diel pH signals along a ~ 0.5 km cross-shore transect in Monterey Bay, California. We deployed small moorings with surface and bottom pH/temperature sensors, sampling at 30 min intervals, from the intertidal to 20 m depth for two weeks in July 2014. We confirmed that there is a clear diel pH signal at the surface, most notable in the intertidal. The signal is described by a maximum pH in the afternoon, corresponding with maximum sunlight availability (and also peak photosynthesis), and a minimum pH in the early morning, when respiration dominates. We found that this signal's amplitude gradates, decreasing from inshore to offshore (*i.e.*, amplitude negatively correlates with distance from shore). Our results show that photosynthesis and respiration are main drivers of diel pH signals near shore. These findings contribute to research that seeks to understand biogeochemical processes in life-sustaining ecosystems—specifically those which are vulnerable to ocean acidification.

INTRODUCTION

Global carbon dioxide (CO_2) levels have risen from approximately 240 ±40 parts per million (ppm) in the 400,000 years before 1800 (Feely et al. 2004) to present day levels nearing 400 ppm (ESRL/NOAA 2014), and are estimated to increase to 1025 ±275 ppm by 2100 (Edenhofer et al. 2014). From 1985 to 2005, the ocean sequestered about 50% more carbon per year than did terrestrial biomes—about 0.6 petagrams (0.6×10^{15}) (Feely et al. 2004). Approximately one million tons of CO_2 enter the ocean every hour (Chavez 2008), which lowers carbonate ion ($CO^{2-}{}_3$) concentrations. Calcifying organisms, such as protists, corals, and mollusks, synthesize carbonate minerals to form their support structures (Feely et al. 2004). Biogeochemists estimate that by 2100, carbonate concentrations and pH will have decreased by 50% and 0.35 units, respectively (Riebesell et al. 2000). Even organisms that tolerate a wide pH range may be close to the limits of their tolerance under "natural" pH fluctuations, so that even a slight decrease in overall pH would have catastrophic consequences for the species (Hofmann et al. 2011). For example, a 0.2 pH-unit decrease in seawater caused 100% larvae mortality in the brittlestar *Ophiothrix fragilis* as a result of skeletal deformation (Dupont and Thorndyke 2009). It is necessary that we learn more about ocean acidification processes near shore, as marine life is concentrated there.

The purpose of this study is to clarify our understanding of nearshore OA processes, with respect to pH, photosynthesis, and respiration. This project addressed the following questions: (Q1) what is the description of surface and bottom diel pH signals near shore? (Q2) Are these signals driven by photosynthesis and respiration? My hypotheses are as follows. (H1) Based on Frieder et al.'s finding that $[H^+]$ was 37% more concentrated at 17m depth, compared to at the surface (2012), I hypothesized that pH will negatively correlate with depth. (H2) Recent work on an NSF-funded project 'OMEGAS' has revealed a clear, diel pH pattern in intertidal zones across 11 sites along the coasts of CA and OR (Chavez, unpubl. data). This signal is described by a daily maximum in pH in the afternoon, corresponding with maximum sunlight (and thus photosynthesis), and a minimum in the early morning when respiration dominates. Data from pairings of intertidal and offshore (≤0.5 km) sensors at 5 of these sites indicate that diel pH amplitude is consistently larger in intertidal versus offshore areas. Based on these findings, I hypothesized that a diel pH amplitude gradient exists from inshore to offshore, and that the amplitude negatively correlates with distance from shore.

MATERIALS/METHODS

To test my questions, I worked with a team from the Biological Oceanography Group at MBARI, led by my mentor Dr. Francisco Chavez. We chose southern Monterey Bay, California, as a test site so we could collect pH/temperature data from MBARI's previously-deployed OA1 mooring (Fig. 1). We deployed eight additional pH/temperature sensors from the intertidal to ~ 0.5 km offshore along the surface and the bottom (Fig. 2). We zip-tied a pH/temperature sensor to submerged railroad tracks in the intertidal. We then deployed three moorings, each consisting of an anchor, line, surface/bottom sensor, and a float, in 100 m increments extending from shore, along a cross-shore transect in line with OA1. Floats functioned to keep bottom sensors ~ 1 meter above bottom (mab) in order to prevent dragging on the seafloor. We tied surface sensors ~ 1 m below the surface at each mooring, where they remained submerged during low tide. Dr. George Matsumoto of MBARI and Dr. Steve Litvin of Hopkins Marine Station assisted by deploying the eighth pH/temperature sensor beneath OA1, about two mab (~ 20 m deep).

With the guidance the Biological Oceanography Group, I assembled these sensors, which consisted of an internally-logging Honeywell Durafet® pH sensor, a cap adapter for amplification, a MadgeTech logger board, a signal conditioning board, separate batteries for the logger board and the Durafet, a copper cap to prevent biofouling, and PVC housing to prevent leakage. I calibrated the sensors to ensure accurate pH/temperature voltage readings. Sampling rate and project duration was every 30 min for two weeks in July 2014, respectively. During these two weeks, I worked with Dr. Kerry Nickols of Hopkins Marine Station, sampling salt, silicate, and pH at each sensor location bi-weekly.

After recovering the sensors, I downloaded their data into MadgeTech, a data analysis program, and converted raw voltage values into actual temperature and pH units, based on each sensor's previous calibration. Using Excel, I made a plot of each sensor's temperature data throughout the two-week duration. This allowed me to confirm that temperature time stamps appeared to be correct (*i.e.*, significant changes in temperature trends lined up, relative to readings from other sensors). I used pH data gathered from the discrete, bi-weekly samples as a check to ensure accurate pH was recorded by each sensor. After determining that accuracy was sufficient (< .05 % ratio difference between discrete and sensor readings), I averaged surface and bottom diel signals for one average day. To do this, I created a spreadsheet with forty-eight half-hour units in one column, corresponding to averaged data points recorded within each half-hour time segment during the two-week period.

I used the salinity, silicate, and pH data collected from discrete sampling to estimate net primary production (respiration and photosynthesis) via DIC (dissolved inorganic carbon) in mg C/m^3/day at each sensor location. This involved inputting average salinity, silicate, and pH values into a program called CO2Sys, which derived DIC content from those parameters.

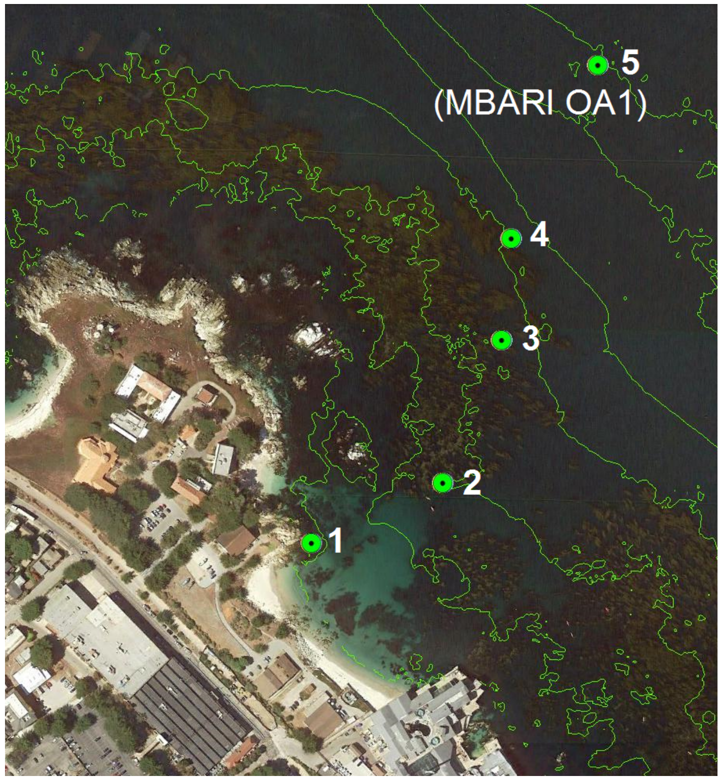

Figure 1. This is an aerial view of the pH/temperature sensor transect, located in southern Monterey Bay, California. Moorings are labeled 1 through 5, from inshore to offshore. The surface sensor on mooring 5 was part of MBARI's OA1 station, which was deployed before the start of this project. The moorings were spaced in approximately 100 m increments extending from shore. Each green contour line radiating from shore represents a 4 m depth increase.

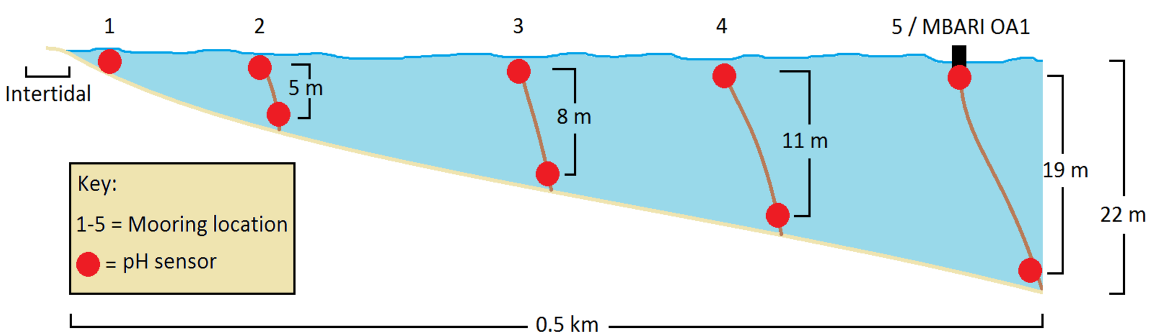

Figure 2. This is a side-view schematic of the transect, showing that vertical spacing between surface and bottom sensors increases from inshore to offshore. Mooring 2 sensors, for example, are 5 m apart, mooring 3 are 8 m apart, and so on. Moorings were spaced approximately 100 m apart from each other in a cross-shore direction, from 1 m to 20 m depths. The numbers 1 through 5 on top correspond to the mooring locations in Fig. 1.

RESULTS

Our results indicate that respiration drives surface pH, most notably in the intertidal. We found that nearshore pH adheres to a consistent diel pattern, which is described by a maximum pH in the afternoon, corresponding with maximum photosynthesis, and a minimum pH in the early morning, when respiration dominates (Fig. 3). Diel pH signal amplitude is largest in the intertidal, and negatively correlates with distance from shore (Fig. 4). A diel signal is apparent on the bottom as well, but corresponds less with sunlight availability than surface signals (Fig. 5). This is to be expected—sunlight availability decreases as depth increases. The bottom sensor on mooring 2 recorded a lower mean pH than any other sensor. We determined that these data were accurate based on pH-test results from the discrete water samples. We speculate that this may be due to a higher level of respiration at this location.

I estimated net primary production (in mg C/m^3/day) on the surface using salt, silicate, and pH data, as well as a program called CO2sys. Table 1 shows the change in net production over the course of an average day at each surface mooring. There is a gradient from inshore to offshore, where primary production changes more per cubic meter inshore. During the two-week deployment, mean pH remained relatively constant, despite temperature increasing about four degrees (Fig. 6).

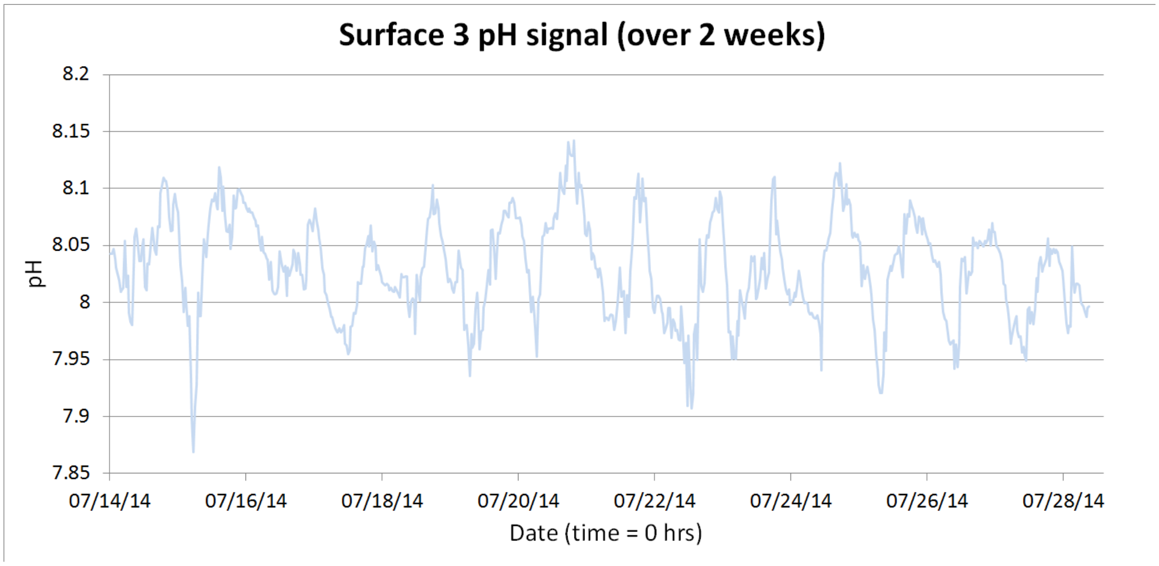

Figure 3: This graph shows continuous pH data from the surface sensor at mooring 3, which was located in the middle of the transect. The Y-axis displays pH, and the X-axis displays the two-week time series.

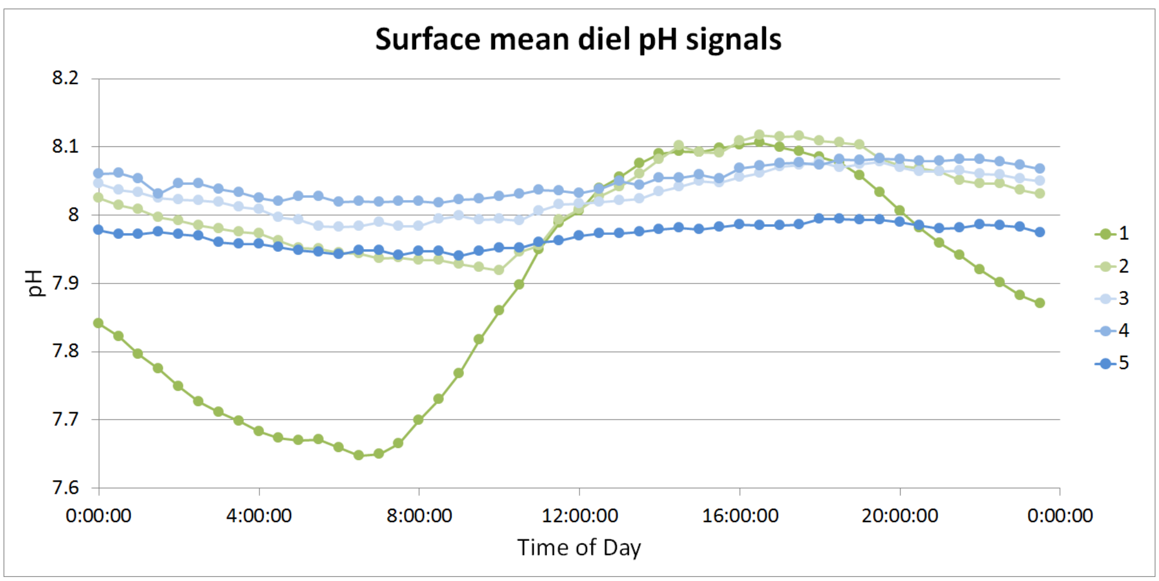

Figure 4. This graph shows average diel surface pH signals. The Y-axis displays pH; the X-axis shows time of day. Raw pH data over two weeks was arranged and sorted into 48 half-hour segments, thus making up a 24-hour day. Numbers 1 through 5 correspond with intertidal to offshore moorings. The lines, color-coded in a green-to-blue gradient, correspond to moorings closer to land (green) versus further from land (blue). Each signal is described by a maximum pH in the afternoon, corresponding with maximum photosynthesis, and a minimum pH in the early morning, when respiration dominates. An amplitude gradient is seen from inshore to offshore, with amplitude negatively correlating to distance from shore.

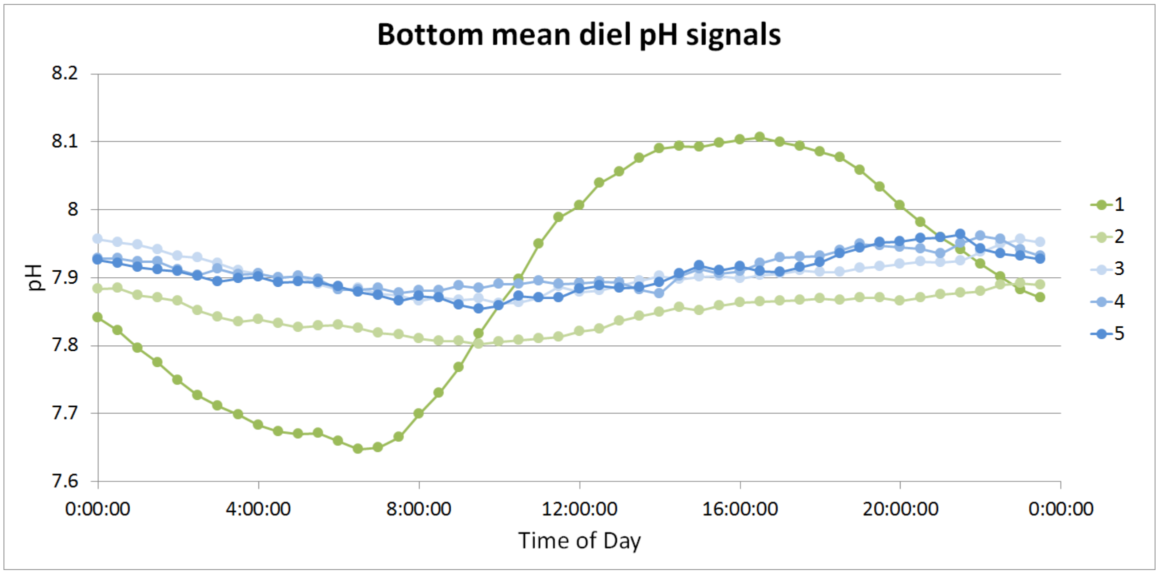

Figure 5. This graph shows average diel bottom pH signals. The Y-axis displays pH; the X-axis shows time of day. Numbers 1 through 5 correspond with intertidal to offshore moorings. The lines, color-coded in a green-to-blue gradient, correspond to moorings closer to land (green) versus further from land (blue). Each signal is described by a diel signal, which is muted compared with surface signals (see Fig. 4). The bottom sensor on mooring 2 recorded a lower mean pH than any other sensor. This may be due to a higher level of respiration at this location.

Mooring	Δ Surface net primary production (mg C/m³/day)
1	2207
2	1110
3	542
4	373
5	289

Table 1. This shows the change in net production (mg C/m³/day) over the course of an average day at each surface mooring. There is a gradient from inshore to offshore, where change in primary production per day negatively correlates with distance from shore.

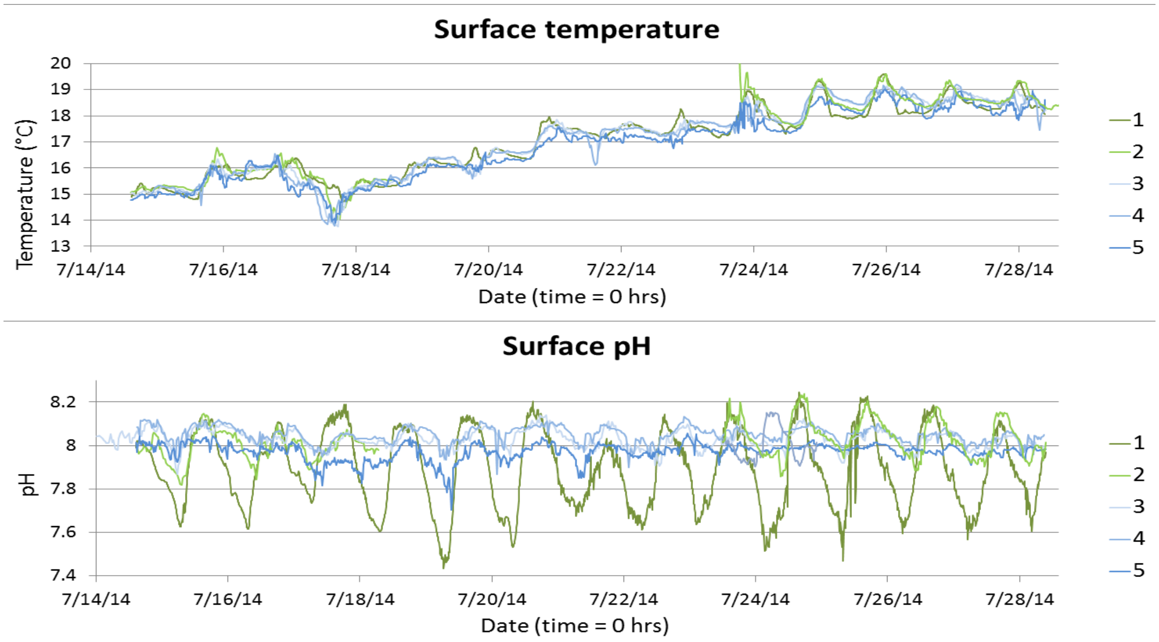

Figure 6. These graphs show a comparison of surface temperature and surface pH. The top Y-axis displays temperature, the bottom Y-axis displays pH, and both X-axes display the two-week time series. Numbers 1 through 5 correspond with intertidal to offshore moorings. The lines, color-coded in a green-to-blue gradient, correspond to moorings closer to land (green) versus further from land (blue). This comparison shows that, despite a significant increase in temperature, pH remained relatively consistent during the project.

DISCUSSION

It is important to understand why we consider net primary production, rather than numerous other variables, to be the most significant driver of nearshore pH signals. During the experimental design of this project, we decided that potential pH-signal drivers could be split into the following two categories: photosynthetic and ocean-mixing. The main photosynthetic variable is sunlight availability. We decided that any effect sunlight availability would have on the separate categories of surface and bottom sensors would be relatively uniform, and thus not relevant to the project. Main variables in the ocean-mixing-variables category are upwelling, current, tide, and wind. In southern Monterey Bay, where the transect was deployed, upwelling events are rare—especially near shore and during the summer. If an upwelling event were to occur, it would not likely cause a diel effect (even if it were to have varied effects on different sensors). Tides cycle twice daily, thus their effect on pH signals would be semi-diel, rather than diel. Currents were observed throughout the two week project, using data from Hopkins Marine Station's ADCP in their Kelp Forest Array. Average currents moved perpendicular to the transect, thus we determined that current would not have a significant effect on nearshore pH signals. Wind velocity increases in the afternoon, thus it is diel. We determined that this variable was not significant because, if wind velocity caused increasing pH in the afternoon, the absence of wind velocity during other parts of the day cannot explain the predictable decrease in pH during the morning. Thus, we determined that photosynthesis and respiration are the major drivers of nearshore pH signals.

CONCLUSIONS/BROADER IMPACTS

We found a clear diel pH signal at the surface, most notable in the intertidal. The signal is described by a maximum pH in the afternoon and a minimum pH in the early morning. We determined that photosynthesis and respiration are the main drivers of this signal, as surface pH is pulled down by respiration in the absence of sunlight. This signal shows up in a gradient from inshore to offshore, where diel change in pH (and thus net primary production) negatively correlates with distance from shore. Results of bottom pH data indicate that the average pH at mooring 2 was lower than the average pH at other moorings. We speculate that this may be the case due to increased benthic respiration near this sensor.

This research fits within the broader goal of understanding pH-related processes near shore, where calcifying, food-web-sustaining organisms are concentrated. The results are relevant to scientists across various fields (*e.g.,* ecology, oceanography, and physiology), policy makers who work in conservation and marine/land-use issues, and any person that benefits from the food and/or capital that these habitats currently—but may not always—provide. Recent ocean acidification research increasingly points us toward the possibility that unless serious recourse is taken with respect to CO_2 emissions, it is not a question if local, regional, and global food webs will be compromised, but when.

As an undergraduate student working on this project, I have acquired practical fieldwork skills (*e.g.,* the ability to assemble/calibrate sensors, deploy/retrieve moorings, operate boats, sample water, and analyze data). I have improved my scientific writing skills due to mentor/graduate student feedback at my host institutions, MBARI and California State University Monterey Bay. My abstract has been accepted at SACNAS, an interdisciplinary undergraduate conference in Los Angeles, which would be a prime opportunity for me to network with professional/graduate school recruiters, as well as expose my work to a diverse scientific audience. This research has better prepared me to engage with academic and public audiences, which will be invaluable throughout my future scientific career.

ACKNOWLEDGEMENTS

This project would not have been possible without support from the following people and organizations: Dr. Francisco Chavez, Dr. Corey Garza, Jeff Sevadjian, Jules Friederich, Christopher Wahl, Marguerite Blum, Dr. Tim Pennington, Dr. George Matsumoto, Linda Kuhnz, Dr. Kerry Nickols, Dr. Steve Litvin, Mary McCormick, Patrick Mulcahy, and the NSF REU program.

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