Changes in Acidification of the Water Column Across the California Coastal Upwelling Front

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March 11th, 2022

Plain Language Summary

Upwelling in the ocean is when water is moved from the deep ocean into the surface waters. There is a natural upwelling zone off the coast of California due to the combination of bathymetry and wind patterns. This upwelled water has a lower pH or is more acidic due to organic matter respiration. In December of 2021, the senior thesis cruise sailed from Honolulu, Hawaii to San Diego, California onboard the R.V. Thomas G. Thompson. Along this transect, the ship stopped at 24 stations to deploy sensors that measure pH, oxygen, temperature, pressure, and salinity. I took water samples from the last five stations at different depths and brought them back to the University of Washington laboratory. I used instruments to calculate pH values directly from the water to compare them to the data from the ship's sensors. Results indicated that the pH values from the bottle samples were slightly more accurate and were used to calibrate the pH data from the ship. The values demonstrated that between the open ocean and the coastal waters, the pH decreased by 0.27. This transition occurred between Stations 14 and 20. At Station 20 on the coast, the pH was 7.78 and in the open ocean at Station 14, the pH was 8.04. A decrease in pH is seen in the location of expected upwelling. Factoring in other properties, such as oxygen, the chemical changes are due to upwelling or respiration.

Abstract

The waters off the coast of California experience upwelling that brings cold, nutrient-rich, relatively acidic waters onto the continental shelf. During the wintertime, this upwelling system creates a front, and the pH of the coastal water demonstrates chemical changes. In December of 2021, the University of Washington's Oceanography senior class went on board the R.V. Thomas G. Thompson that sailed from Hawaii to San Diego. During this transect, the rosette was deployed 24 times. The sensors on the rosette measured the pH of the water column. This data was analyzed and compared to bottle samples taken from the Niskin bottles at the last five stations. The results of the pH analysis show the transition between Station 14, within the subtropical gyre, and 20, on the continental shelf. The pH values between these two stations decreased by 0.27. At 200 m, the pH values were 8.05 and 7.78 for Station 14 and 20, respectively. Along isopycnals, the coastal waters were found to be more acidic than those offshore - reflecting either respiration or upwelling. The pH values at this location have not noticeably decreased in the last couple of years, but the data does not go back far enough.

Introduction

The increase of anthropogenic CO_2 in the atmosphere has created many issues for the Earth. One major impact on the oceans is the increase in acidification. Acidification is when the pH of water decreases otherwise known as becoming more acidic (Feely et al. 2004). Further, a lower ocean pH leads to a decrease in carbonate ions which makes it difficult for shell-building organisms and other marine organisms to survive. These organisms, such as mussels and other shellfish, are a vital part of many people's diets. Other organisms that use calcium carbonate are phytoplankton. For example, coccolithophores use calcium carbonate to build their shells. Phytoplankton also performs almost half of the earth's photosynthesis, creating the oxygen all organisms use to respire. Other organisms are corals which create reef ecosystems that provide shelter for fish and protect coastlines. Ocean acidification is caused by chemical reactions between seawater and carbon dioxide. The following equations explain the chemical process thoroughly:

Gaseous CO_2 in the atmosphere is dissolved into water to be at equilibrium:

$$CO_{2\,(g)} + H_2O_{\,(l)} \quad CO_{2\,(aq)}$$

The CO2 and seawater then react to yields bicarbonate and hydrogen ions:

$$CO_{2\,(aq)} + H_2O_{\,(l)} \quad H^+_{(aq)} + HCO^-_{3\,(aq)}$$

Then more bicarbonate is formed due to carbonate and hydrogen ions reacting:

$$H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \quad HCO^-_{3\,(aq)}$$

The entire reaction between carbonate and carbon dioxide:

$$CO_{2\,(g)} + H_2O_{\,(l)} + CO_3^{2-}{}_{(aq)} \quad 2HCO^-_{3\,(aq)}$$

The addition of carbon dioxide to the oceans causes the reactions above, and the first step is instantaneous. With increased carbon dioxide fluxing into the ocean, the waters become more acidic, because more H^+ ions drive the pH down (Osborne et al. 2020). The pH of the California Current System in 1750, before the beginning of the industrial revolution in 1760, was 8.12. In 2005 the pH was 8.04, showing a significant decrease due to anthropogenic factors (Gruber et al. 2012). However, in 1750, in the coastal region of California, the pH was already measured at 8.03. This demonstrates a natural upwelling of acidic water. In 2005, with natural acidification due to upwelling waters and increases in anthropogenic CO_2, the pH at this location was 7.95 (Gruber et al. 2012).

Natural zones of acidification are caused by earth processes such as upwelling. The process of upwelling is generated by wind blowing along the coastline. Another process is the Ekman transport which is a force due to drag. Similarly, the Coriolis force causes water movement to the right in the Northern Hemisphere, driven by the Earth's rotation. The wind off of the coast of California moves the surface waters south. Then, the Coriolis force transports the water to the offshore (Huyer et al. 1983). Simultaneously, the Ekman transport moves the surface water column. Thus, the coastal waters are being pushed away from the coast and new deep-sea water comes up to replace it (Black et al. 2011).

The upwelling off of the coast of California creates a front between the open ocean and land. A front is apparent due to the sharp vertical gradient that has changes in water properties from depth to the surface. The California current front is caused by the continental shelf and the average wind direction (Kahru et al. 2018). The continental shelf is the edge of the land continent under water which is short and steep on the West Coast of the North American continent. When water here is upwelled, it is brought to the surface and onto the California Coast (Huyer et al. 1983). The winds in the region blow stronger offshore during the summertime, so upwelling is increased in the summer and declines in the winter (Black et al. 2011). The front's strength

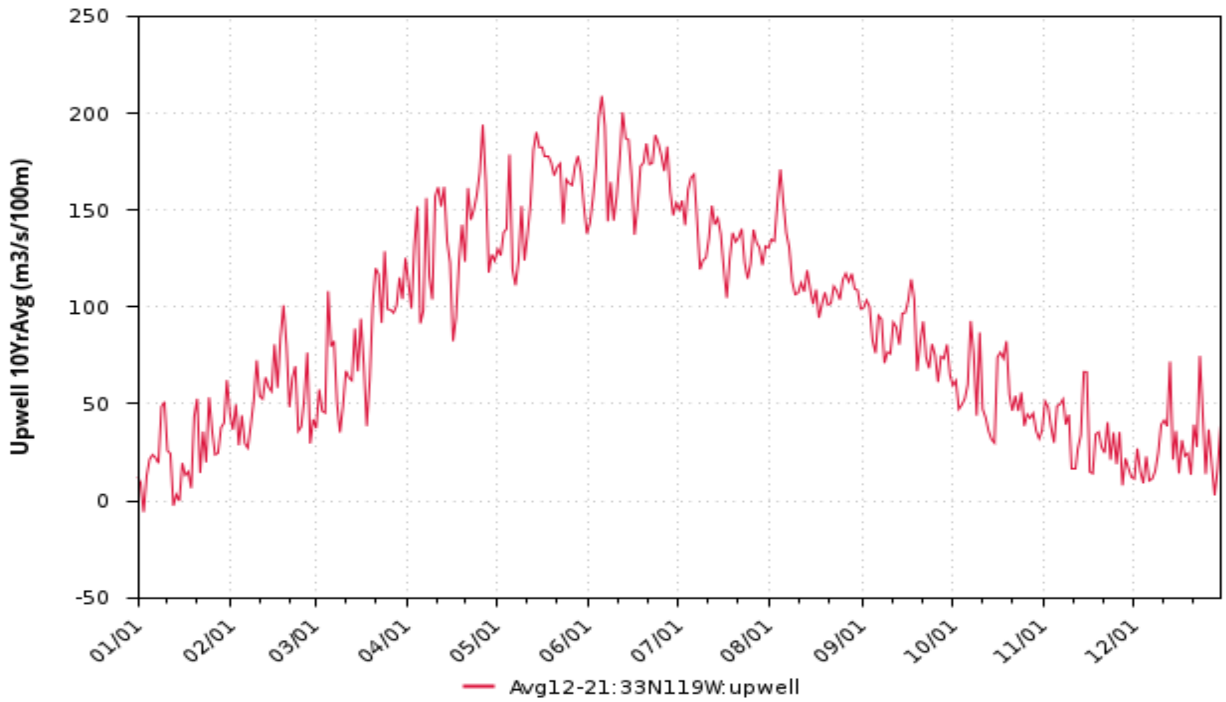

Figure 1: Pacific Ocean Upwelling Index off of the coast of California, west of San Diego. Monthly upwelling index averaged over the last ten years from 2012 to 2021 (http://www.cbr.washington.edu/dart/query/upwell_daily).

varies seasonally due to these changes in upwelling. The upwelling magnitude seasonally averaged over ten years shows these seasonal fluctuations (Fig.1). The average upwelling in the summer reaches an index of 200 m3/s/100m. The highest upwelling occurred between May and August and then declined with the lowest index from November to February.

In December of 2021, the upwelling index ranged from 75 m3/s/100m to 2 m3/s/100m (Fig. 1). During the winter, upwelling remains apparent with a decreased magnitude. The seasonal variability of upwelling changes the acidity of the waters on the coast of California.

Upwelling can change the acidity of surface water, since it transports deep water with a low pH into surface waters. There is a seasonal and yearly variation of pH with the lowest pH values measured in the summer (Leinweber and Gruber 2012). Between 2003 and 2008, The Southern California Current System near Santa Monica was analyzed for trends using dissolved

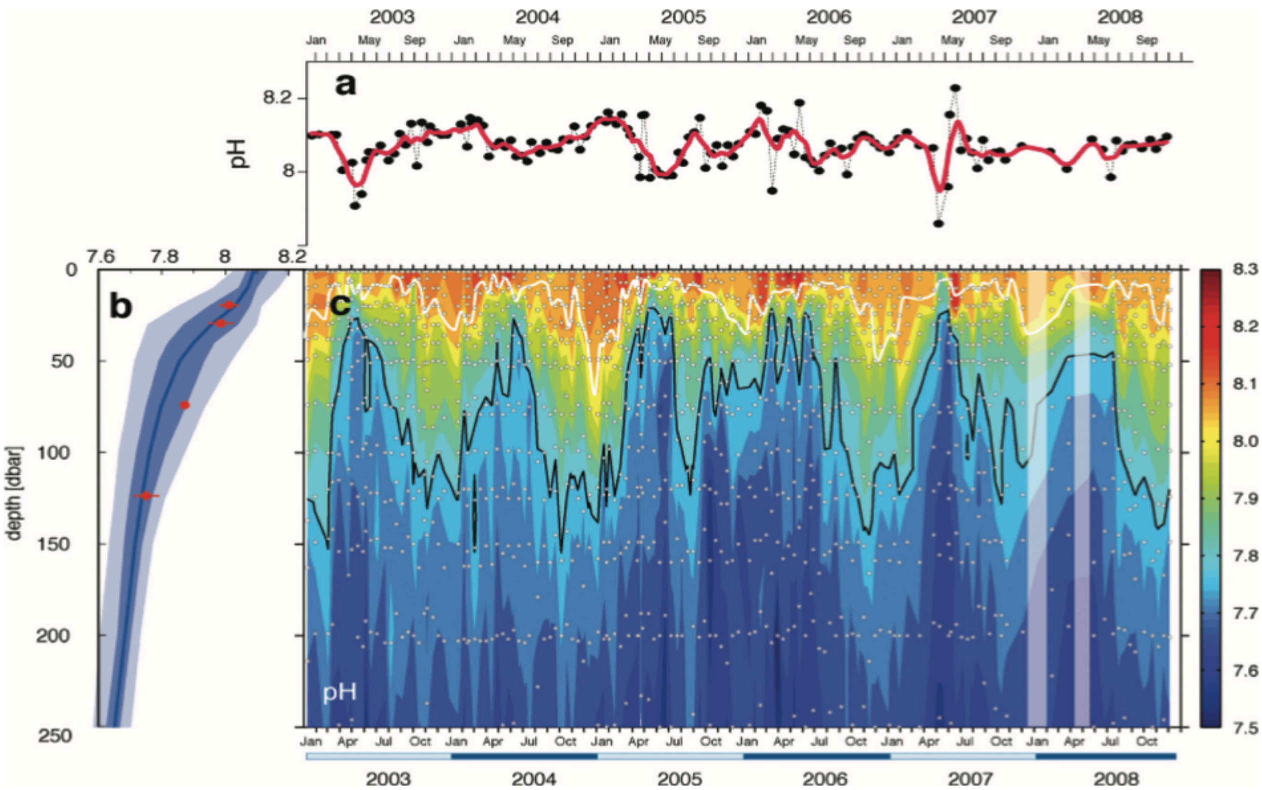

Figure 2: Santa Monica bay observatory Mooring (33° 56′ N, 118° 43′ W) data from 2003 to 2008. Panel a: average pH over top 20 m with the red line being a 45 day mean. Panel b: median profile for pH with quartiles (25-75% and 5-95% in the light shades and dark shades respectively). The red dots are mean values. Panel c: pH over six years plotted with time and depth. Dots are measurement locations, the white line is the mixed layer depth, and the black line is the saturation horizon of aragonite (Leinweber and Gruber 2012).

inorganic carbon and alkalinity (Fig. 2). The pH changes in the region of the front affect the coastal waters. The naturally shallow coastal waters on the continental shelf and the upwelling process create changes in the chemical properties of the surface waters. Along the front, there is older water brought up from depths that is more acidic because of respiration. When water is in the deep ocean for an extended period of time, organic matter respires and creates carbonate causing the pH to decrease. When this acidic water is brought up to the coast and mixed with the surface water, the pH on the coast decreases.

Previous assessments of the California Current system show the pH of the water has decreased by 0.1 since the time of the industrial revolution (Hauri et al. 2009). The decrease in pH was expected to be seen in several decades but is significantly low for surface open ocean waters today. The acidification occurring here is happening quickly due to the upwelling processes and atmospheric increases in carbon dioxide. The upwelled waters are coming up from the deep ocean, though they have still been in contact with the atmosphere in a recent time scale. The California Current Systems average estimation for transit is 40 to 50 years (Feely et al. 2008). Thus, these waters have exchanged with the atmosphere during the industrial period. The exchange would drive the water's pH down further if the initial pH was more acidic (Hauri et al. 2009).

Deployments of gliders were used to collect more data near the California coast in hopes to further understand these patterns. A survey of the front was done in northern Monterey Bay in the Spring of 2012. A chemical gradient was found in the summer months using gliders that were 20-50 km offshore of California (Fig. 3). The glider data collected by the surveys demonstrate the offshore front and its changes in water properties. In the

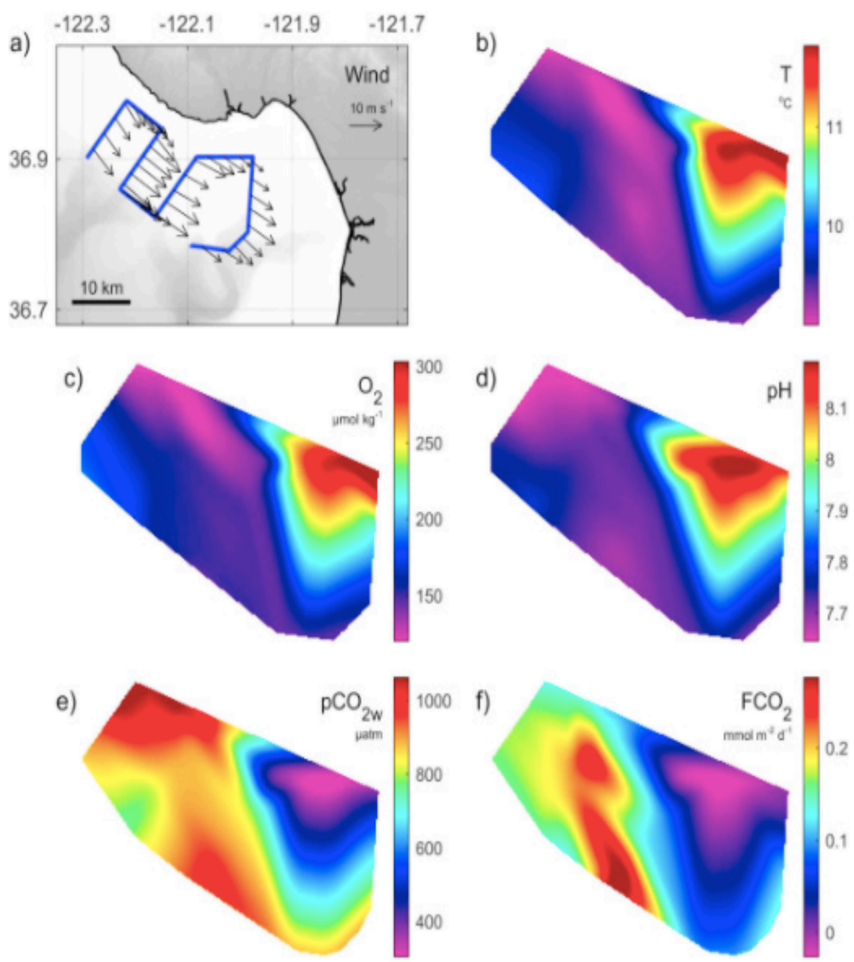

Figure 3: Glider survey off of the California coast, in northern Monterey Bay. Panel a: glider paths location at sea surface. Panel b: temperature. Panel c: dissolved oxygen. Panel d: pH. Panel e: pCO2. Panel f is FCO2 (Chavez et al. 2017).

open ocean region of the front, there is upwelling which brings up the cold water that is depleted in oxygen and has a low pH. The water in this region has higher dissolved carbon dioxide due to less production at depth. On the other side of the front, near the coast of California, there is a drastic change in water properties with the temperature, oxygen, and pH increase. The dissolved carbon dioxide, however, is being used up by primary producers, causing it to decrease. These surface waters change in properties within a small distance, which defines the front off of the California Coast (Chavez et al. 2017).

Recent cruises near the US West Coast and the northern Gulf of Mexico have collected oxygen and pH data to compare changes in chemistry. The in situ pH_T was plotted against dissolved oxygen and demonstrated a significantly positive linear relationship. The data from this study concluded that water column acidification is enhanced by the respiration of organic matter (Feely et al. 2018).

The goal of this study is to collect data that supports my hypothesis. My hypothesis is that there is a decrease in pH on the California coast due to upwelling which causes acidification. From the subtropical gyre to the California coast, there will be a transitional front. The pH observed here will show an increase in acidity compared to previous years. The chemical water properties at the front will be high in pCO_2 and nutrients, whereas the temperature, oxygen, and pH will be low. The chemical changes are due to upwelling and the magnitude will be decreased due to the winter season but the contrast from the open ocean to the coastal waters will still be significant. The pH calculated in the lab will be more accurate than the data from the ship and will be useful to calibrate the accuracy of the ship's data.

Methods

The research cruise collected data along a transect from Hawaii to San Diego. The cruise transect included 24 stations and I utilized data from 23 of them (Fig. 4). The focus of this study was on the California coastal upwelling front. In this region, the station spacing after Station 19 was reduced from 2 to 1 degree of longitude. Stations 20 to 24 are on the continental shelf of the North American continent offshore of San Diego, California (Fig. 4). At each station, a rosette with a Sea-Bird Model SBE 9 CTD, Sea-Bird SBE 43 dissolved oxygen sensor, Sea-Bird SBE 27 pH sensor, and 24 10-l Niskin bottles were deployed. These collect in situ data and water samples for discrete analyses of dissolved compounds. From the CTD sensor, I used pressure, temperature, and salinity, which I then used to calculate density.

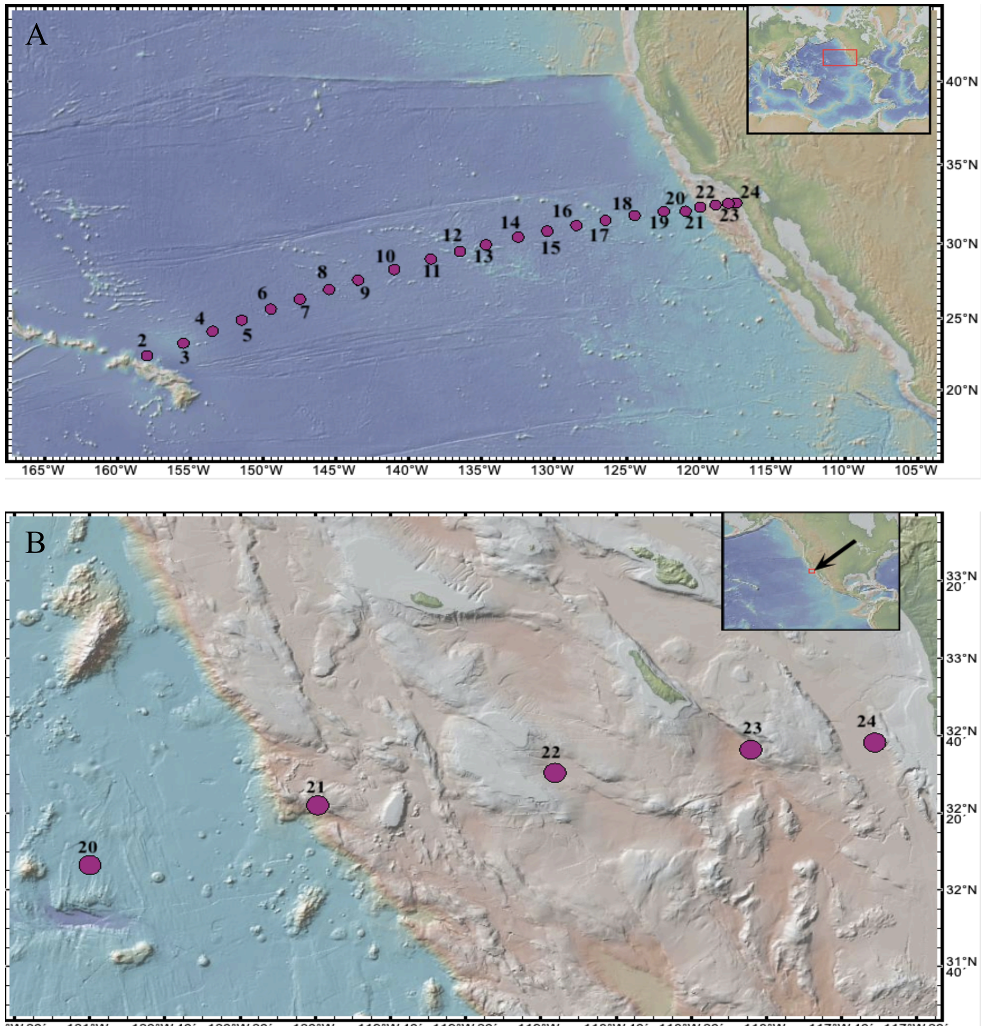

Figure 4. Senior thesis cruise track. Panel A: stations from Hawaii to San Diego (2-24). Panel B: cruise track zoomed into the California Coast to show the last five stations (20- 24).

Bottle samples were collected from the 24 10-1 Niskin bottles at these five stations by filling up glass bottles with water. Each had a specific depth from the surface water of 5m to 500m. The twenty-four bottle samples from the cruise were all poisoned immediately after being collected with mercuric chloride to prevent biological processes from changing the chemistry of the water. Running the bottle samples in the Gagnon Laboratory, I measured dissolved inorganic carbon and total alkalinity. The total dissolved inorganic carbon in seawater was measured using a Single Operator Multi-Parameter Metabolic Analyzer or SOMMA. The total alkalinity in seawater was measured using an open-cell titration (Dickson et al. 2007). Based upon these two parameters, I calculated pH using the CO2SYS program (Pierrot et al. 2006). The program takes any pair of alkalinities, pCO_2, and pH to calculate chemical properties. I used TCO2 and alkalinity in addition to salinity, temperature, and pressure to calculate pH. The accuracy of the pH measurements from the sensor is understood by plotting the two pH values against each other. The R squared value is 0.9388 and the equation is pH Calculated = 1.1542 * pH Sensor - 1.2657 (Fig. 5). This relationship was applied to the pH sensor data for calibration.

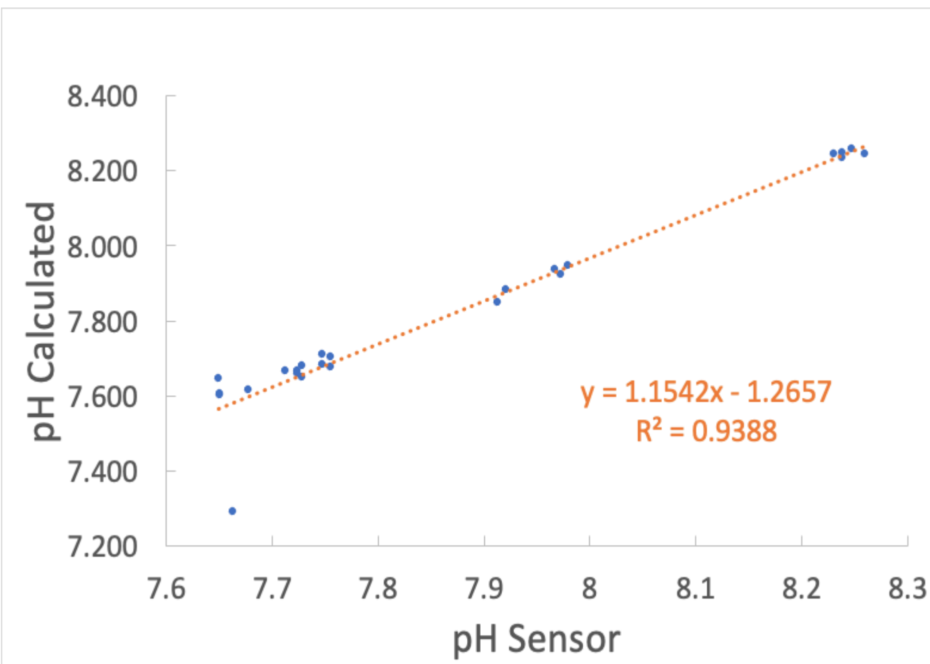

Figure 5. Calculated in lab pH values plotted against Rosette's pH sensor values.

Results

Bottle sample data ran in the lab analyzed for TCO2 and Alkalinity. The TCO2 is similar for the last five stations. Station 2 or station Aloha, however, shows the differences in TCO2 values near Hawaii (Fig. 6A). The TCO2 values are greater near the California Coast compared to Hawaii. There is scatter in the surface alkalinities which disappears at the samples from 300m and 500m (Fig. 6B).

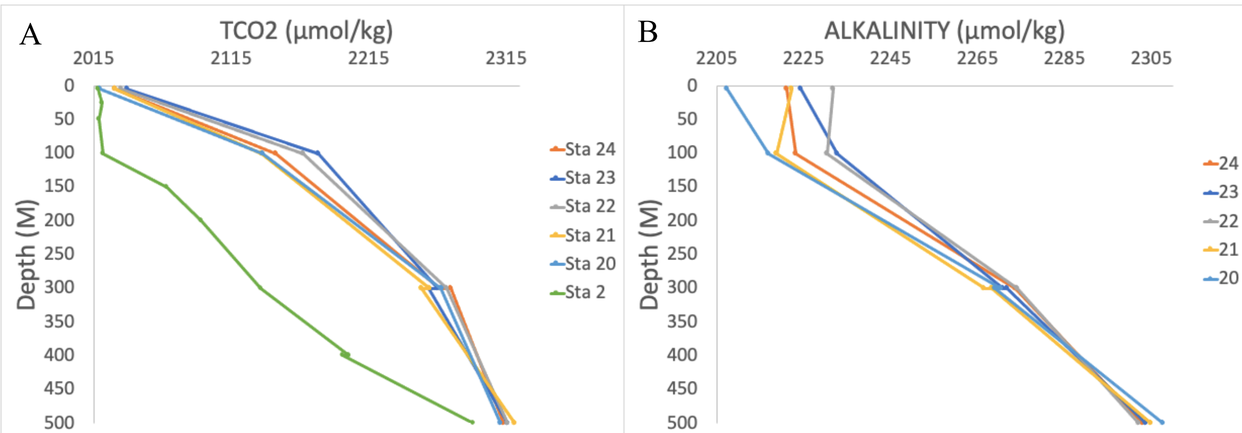

Figure 6. Panel A: TCO2 in plotted against depth. Panel B: alkalinity plotted against depth. The legend shows stations 20-24, which are the last five stations near the California coast. Station 2 is at Station Aloha which is North of Oahu, HI. Bottle samples taken from Niskin bottles on rosette deployments from 5m to 500m.

The pH sensor data from rosette deployments on the cruise. The vertical profiles of pH from the 23 stations reveal some common features and important differences. The pH at every station decreases with depth. At the surface the pH is between 8.1 and 8.3 and the pH at a depth of 600 meters is between 7.5 and 7.7 (Fig. 7A). The pH values decrease when approaching the coast. The last five stations, closest to the coast of California, are the most acidic. The pH values continue to decrease when plotted against potential density or Sigma Theta (Fig. 7B).

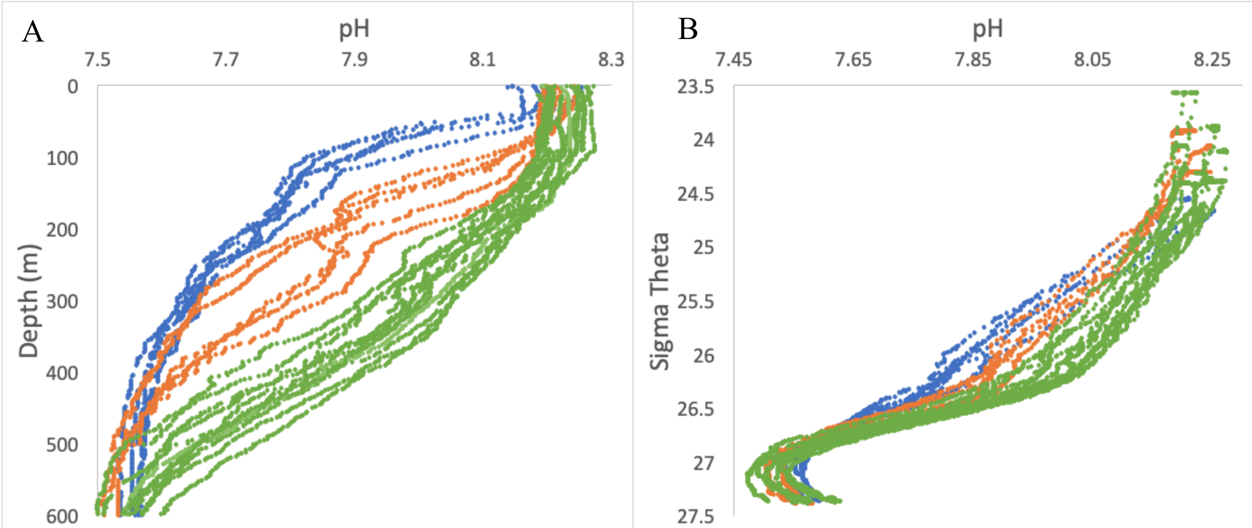

Figure 7. Panel A: pH plotted against depth at each station. Panel B: pH plotted against Sigma Theta or a quantity used to measure the density of seawater. The values are from the sensor on the rosette during the cruise and are calibrated with the equation from the bottle sample analysis. The station numbers 2-24 are grouped in color. Green: Stations 2-14, Orange: stations 15-19, Blue: Stations 20-24. The samples are from CTD casts from the surface to 500 meters.

The oxygen concentrations decrease with depth below the mixed layer. The oxygen values at the surface are between 208 µM/kg and 254 µM/kg. At depth, the values are between 10 µM/kg and 60 µM/kg (Fig. 8A). The oxygen values closest to the coast are the lowest at depths below 50m and highest in the surface waters above 50m. The oxygen values continue the same trends when plotted against Sigma Theta or density (Fig. 8B).

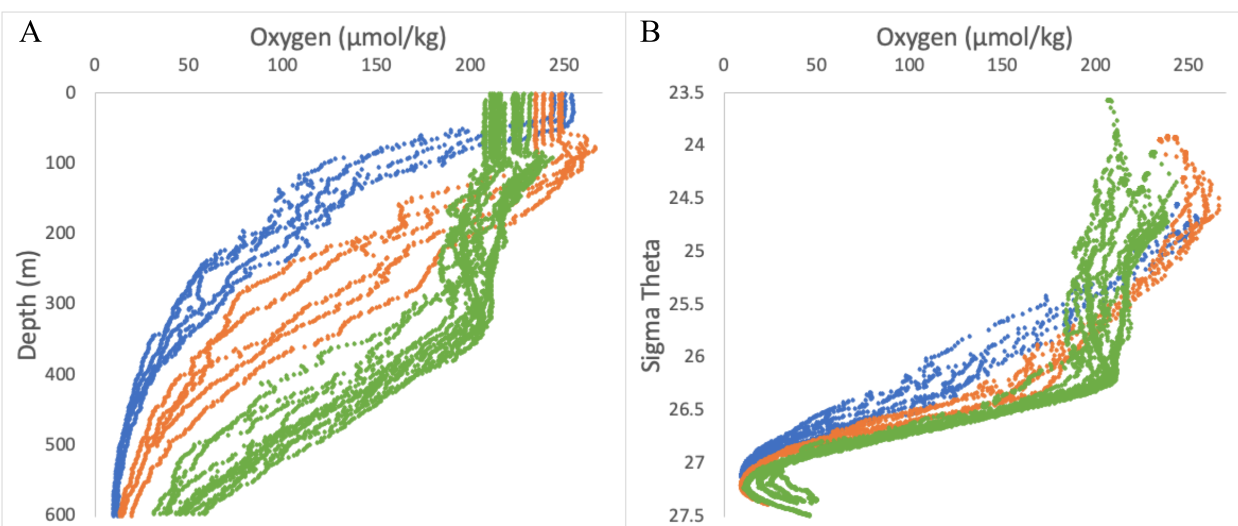

Figure 8. Panel A: Oxygen plotted against depth at each station. Panel B: oxygen plotted against Sigma Theta or a quantity used to measure the density of seawater. The values are from the sensor on the rosette during the cruise and are calibrated with the equation from the bottle sample analysis. The station numbers 2-24 are grouped in color. Green: Stations 2-14, Orange: stations 15-19, Blue: Stations 20-24. The samples are from CTD casts from the surface to 500 meters.

Discussion

The results from the data show three separate zones: subtropical gyre, transition, and coastal. Stations 14 to 19 show a transitional stage with pH values at 30 m depth from 7.86 to 7.65 (Station 15 and 19 respectively). Stations 2-14 have a pH range from 8.0 to 7.9 at 300m depth (Stations 4 and 14 respectively). The last five stations (20-24) have a pH range from 7.65 to 7.62 at 300m depth (Fig. 7A). The transitional region shows that there is a change in chemical properties occurring at this location. In contrast, the stations in the gyre have higher pH values than those on the other side of the transition. The stations near the coast after the front have more acidic waters. The oxygen values decrease at the same stations (Fig. 8A). Stations 15-19 show a decrease in oxygen from 156 µM/kg at Station 15 to 74 µM/kg at Station 19. The oxygen values in the gyre are higher at 300m than those on the coast. Oxygen and pH decrease near the coast of California in the same regions. A transitional front is passed from the subtropical gyre to the California coast.

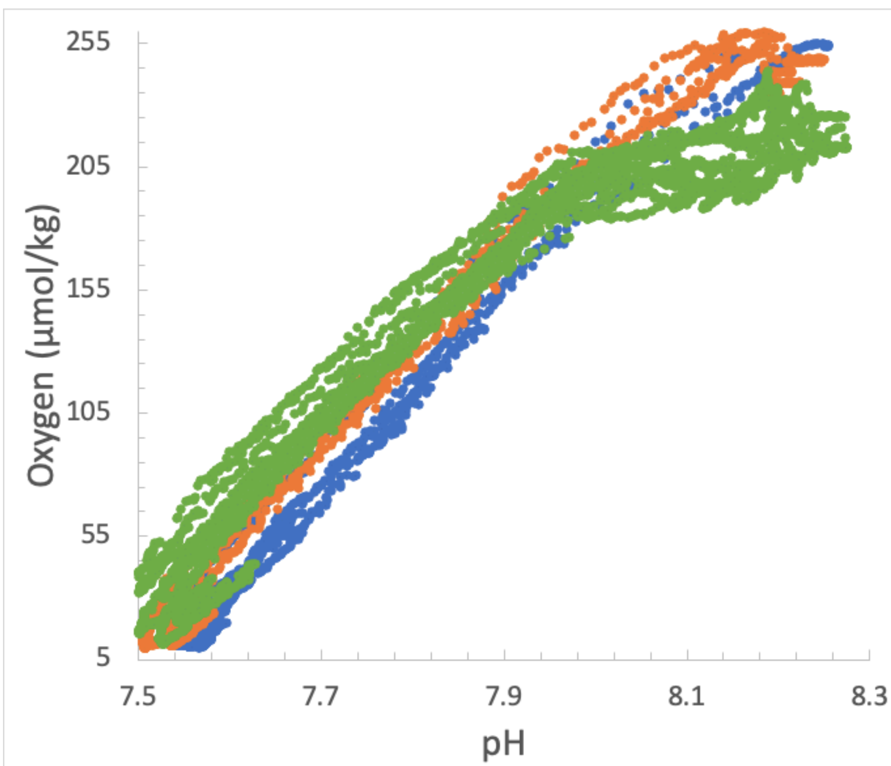

Figure 9. Oxygen plotted against pH from sensors. The station numbers 2-24 in the legend and are grouped in color. Green: Stations 2-14: Orange: stations 14-19: Blue: Stations 20-2. The samples are from CTD casts from the surface to 500 meters.

The pH and oxygen plotted against Sigma Theta, otherwise known as a measure for the density of seawater, demonstrate that the observed changes in pH and dissolved oxygen are not due to isopycnal surfaces getting shallower. Other factors affected the water properties such as respiration and upwelling. The oxygen and pH values decrease due to the process of upwelling (cross-isopycnal mixing) or respiration. The change in oxygen and co-located decrease in pH on isopycnals are consistent with a respiration signal. Oxygen is lower on the shelf at specific pH values (Fig. 9) and responds quicker than pH. It may also be that the pH is a logarithmic quantity so the expected change in pH would be smaller than detected. The respiration of organic matter reduces dissolved oxygen and produces CO2 in an approximately equal molar ratio. The expected change of pH due to the respiration signal measured would be 0.05 (Feely et al. 2018).

This increase in acidity is a natural process due to upwelling. The values change seasonally and in December the upwelling index is lower. I can compare our measured pH to those from the previous study (Leinweber and Gruber, 2013) using the Santa Monica bay observatory Mooring (33° 56′ N, 118° 43′ W). The pH at a depth of 100m in December of 2003 is 7.85 and in December of 2007, the pH is 7.75. The pH from our December cruise at 100m depth at this longitude is around 7.8 at Station 23. Comparing 2021 to 2003 there is a slight decrease in pH. However, it is not significant when looking at the pH fluctuation of 2007. The upwelling index in December of 2003 was between 190 and -260 m3/s/100m. The upwelling index in December of 2007 was between 200 and -40 m3/s/100m. The changes in pH are highly affected by the amount of upwelling that occurs. During my data collection, the upwelling index was between 130 and -50 m3/s/100m. The upwelling in 2003 was overall weaker than in 2021, and the pH value was higher. The upwelling in 2007 was the strongest and correlates to the lowest pH value. The other years in this study are all around a pH of 7.8 but in 2004 there is an increase to a pH of 8. More history of the pH at this region would be needed to make further conclusions on if there is an anthropogenic contribution to the decrease in pH.

Conclusions

The pH values decrease in the water column and from the subtropical gyre to the California coast. Off of the coast of California, there is a chemical front created by upwelling. This is seen in changes in chemical properties in the water such as oxygen and pH. The oxygen and pH values both decreased going toward the coastline and the greatest transition was between stations 14-20. This is due to upwelling or respiration and not due to density. The waters at depth are naturally acidic because of organic matter respiration so the water being upwelled has a lower pH and creates a more acidic environment on the coast. The pH data in this location only goes back twelve years and does not show any conclusive trends that there is acidification occurring due to changes in the climate. Studies could be done to separate the changes in pH from natural acidification due to upwelling and anthropogenic acidification. Additionally, further studies could be done to observe if the water being upwelled is more acidic due to anthropogenic effects. Overall pH should continue to be studied to gauge acidification along the California coast to prevent harmful effects on the marine environment.

Acknowledgments

Thank you to the R.V. Thomas G. Thompson crew for having us on their ship. To the cooks and staff for making it comfortable and to the science crew for teaching us new skills. Thank you to the professors for guiding us through the last seven months and my advisor Mark Warner, for all the support. A special thank you to my classmates for all the advice and help.

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