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Ocean acidification in the Eastern Tropical North Pacific

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NONTECHNICAL SUMMARY

Since the beginning of the industrial revolution about 250 years ago, atmospheric carbon dioxide (CO_2) concentrations have been increasing steadily as a result of humans burning fossil fuels, wood, and coal. As the atmospheric CO_2 concentration increases, approximately 30% of it will end up in the oceans, causing chemical changes to the ocean basins. The Eastern Tropical North Pacific (ETNP) has a large region of water with less than the average oceanic concentrations of dissolved oxygen present in the water column. These regions are commonly referred to as oxygen minimum zones (OMZs), and they are creating nearly anoxic—with no oxygen remaining--water south of Cabo San Lucas, Mexico. The ETNP OMZ is expanding, causing an increase in CO_2 concentrations and a steadily declining pH in the region. As oceanic pH continues to decline, the water undergoes ocean acidification, causing calcium carbonate ($CaCO_3$) shelled organisms to have increased difficulty forming their shells. In the data collected from the ETNP in late March, 2012, the pH ranged from 7.49 off the coast of San Diego, CA to 7.39 near the center of the OMZ at a depth of 800 meters. More data collection in this region is required to gain an appropriate overview of the effects of ocean acidification on the ecosystem as a whole.

ABSTRACT

Over the last 250 years of human development upon the Earth, the global anthropogenic carbon dioxide (CO_2) input has continued to increase as a result of the burning of fossil fuels, wood, and coal (Feely, 2004). As the atmospheric CO_2 concentration increases, the ocean continues to absorb approximately 30% of it (Sabine, 2007). When CO_2 is absorbed into the ocean, it forms carbonic acid (H_2CO_3) and causes the oceanic pH to decrease (Doney, 2009). In the Eastern Tropical North Pacific Ocean, there is a large oxygen minimum zone (OMZ) spanning from a depth of approximately 50-1,000 meters (Carl, 2012). In the OMZ, the respiration of CO_2 from marine bacteria into the water column, further decreases the pH and makes it more difficult for calcium carbonate shelled organisms to survive (Feely, 2008). In March 2012, water samples were collected from 20 locations at multiple depths along three transects of the ETNP, along the western coast of the Baja peninsula, from the south end of Baja toward the Mexican mainland, and then straight inland to Manzanillo, Colima. Along the Baja transect, the pH values in the water column were close to the average values--between 8.05 at the surface and 7.35 at a depth of 1,000 meters in the central North Pacific Ocean (Byrne, 2010). Further south from the Baja transect the pH decreased as much as 0.258 units below expected values calculated for the pH change that the OMZ caused.

The marine carbon cycle describes the fluxes of carbon dioxide (CO_2) between the oceans, terrestrial biosphere, lithosphere, and the atmosphere. Since the beginning of the industrial revolution in the early 20th century, atmospheric CO_2 has increased by nearly 40%. The global oceanic reservoir acts as a sink for about one-third of the atmospheric CO_2, and as a result of the rising concentrations, the global oceanic chemistry is changing (Doney, 2009).

The carbon cycle involves both organic compounds as well as inorganic carbon compounds. The inorganic compounds are particularly relevant when discussing ocean acidification, as it includes the many forms of dissolved CO_2 present in the oceans: carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). Atmospheric CO_2 dissolves in seawater and is hydrated to form H_2CO_3, which is can undergo two de-protonation reactions to form HCO_3^- and CO_3^{2-}. The co-existence of these species in seawater creates a chemical buffer system, regulating the pH and the CO_2 of the oceans (Orr, 2005).

Increasing CO_2 concentrations in the water column will decrease the pH simultaneously, making pH measurements ideal for tracking the changes to the water chemistry over short periods of time. Other factors, such as dissolved inorganic carbon and alkalinity do not change as rapidly as pH, but are still needed to give a more accurate picture of the ocean chemistry.

In oceanic upwelling zones, such as the Eastern Tropical North Pacific, there are increased CO_2 concentrations and decreased pH values. The increased CO_2 concentrations also correlate to a region of near anoxic conditions, where there is not enough oxygen deeper than the surface mixed layer in the water column for many aerobically respiring organisms to survive. Aerobic respiration is defined as:

$$CH_2O + O_2 \rightarrow CO_2^- + H_2O \qquad [1]$$

This chemical formula shows that when an organism breathes O_2, it produces CO_2 and water, which reinforces the cycle of decreasing O_2 with decreasing pH in the water column.

Deeper than the oxygen minimum zone (OMZ), denitrifying bacteria thrive on the sinking organic particles and respire more CO_2 into the water column, causing the pH to continue to decrease with depth. Denitrification, or anaerobic respiration is defined as:

$$4\ NO_3^- + 5\ CH_2O + 4H^+ \rightarrow 2\ N_2 + 5\ CO_2 + 7\ H_2O \qquad [2]$$

This chemical formula shows that bacteria are consuming nitrate (NO_3^-) and hydrogen (H^+) ions to form ‘fixed’ nitrogen gas (N_2), CO_2, and water, reinforcing the cycle of decreasing NO_3^- with decreasing pH in the water column.

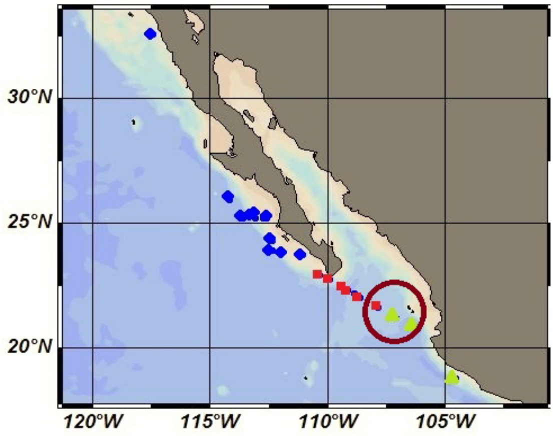

Figure 1: All sampling locations. The circle indicates where there is an underwater current present (Spencer, 2012).

METHODS

Sampling for this research project occurred at twenty locations in the Eastern Tropical North Pacific region from San Diego, California, USA to Manzanillo, Colima, Mexico (Figure 1) while aboard the *R/V Thomas G. Thompson* from March 17th-27th, 2012 using a 24-niskin rosette and CTD to collect discrete water samples from throughout the water column. All water analyses were conducted while underway.

A Mettler-Toledo auto-titration device was used to analyze up to 9 20mL water samples at a time. Using the program LabX with the autotitrator, the data is collected to accuracy better than 0.1% relative standard deviation (Mettler-Toledo). A pH meter was attached to the device and 10 samples of each of the pH standards were measured to ensure the accuracy of the data collected (Appendix 1). The pH of each water sample was promptly measured to prevent atmosphere-water interactions which could alter the pH readings. This device uses an automated gran-titration program to determine the total alkalinity of each sample. In order to ensure the accuracy of the titrations, triplicates were run from each sampling depth.

The pH and alkalinity values were then used to solve for the total dissolved inorganic carbon (DIC) and the total CO_2 using the chemical equations given in James W. Murray's "Ocean Carbonate Chemistry: The Aquatic Chemistry Fundamentals".

RESULTS

The changes in pH with depth are from 8.15 to 7.30 in the top 250 meters of the water column. The correlation between decreasing pH and depth is $y=-1103pH + 8721$, with an $R^2 = 0.5$. In the transect running along the west shore of the Baja peninsula, the pH drops from 8.06 at the surface to 7.09 at 320 meters depth. The pH changes from 8.15 at the surface to 6.71at 800 meters in the transect running from the tip of the Baja peninsula to the mainland of Mexico in the east. The final transect was closer to the mainland and accompanied by much lower surface pH values, starting out near 7.50 at the surface and dropping down to 6.78 at a depth of 1000 meters.

When comparing the pH with changing O_2 concentrations (Figure 2b), there is a connection between decreasing O_2 and decreasing pH values. Along the transect of the coast of Baja, the relationship between pH and O_2 appears to be linear until the oxygen reaches nearly 0µmol/kg. At this point, the pH continues to decrease from about 7.4 to 7.1 in the anoxic water. The transect crossing the Gulf of California follows the same O_2 slope with decreasing pH as the Baja transect, but reaches a 0 µmol/kg O_2 concentration at pH 7.6 and then drops to below 7.0. The coastal region did not have any O_2 concentrations greater than 96µmol/kg with a pH ranging from 7.5 down to 6.8. The pH values are nearly equal in the coastal region for water with 96µmol/kg O_2 and nearly 0µmol/kg present.

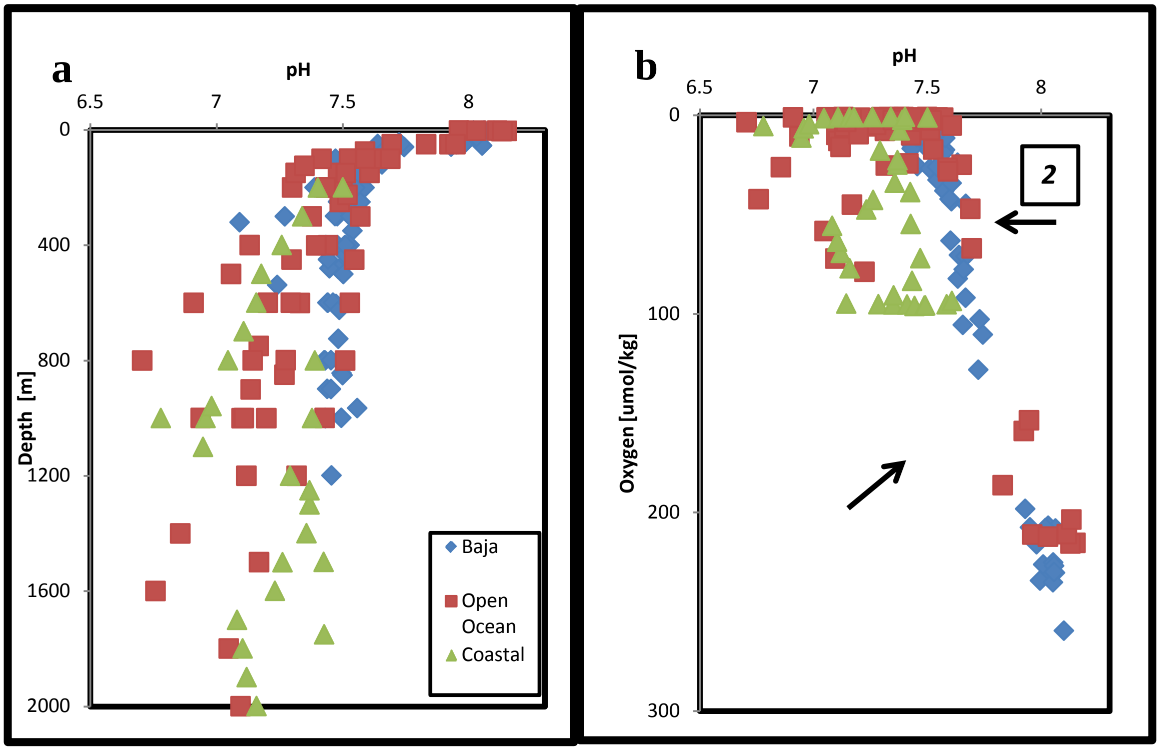

Figure 2. Changing pH as a result of a) increasing depth and b) decreasing oxygen.

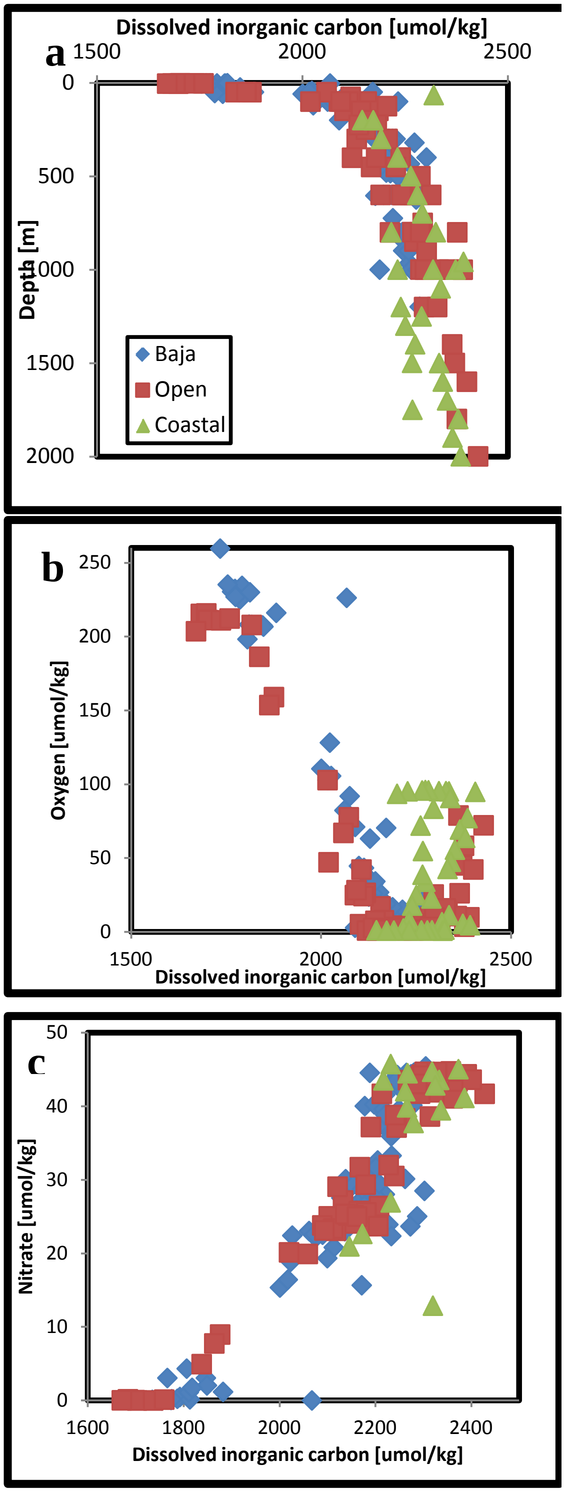

Figure 3. Changes in dissolved inorganic carbon (DIC) concentrations as a function of a) depth, b) O_2, and c) nitrate.

Figure 3 shows three variables compared to dissolved inorganic carbon (DIC). In 3a, DIC increases with depth over all three transects of the ETNP. In the surface to 200 meter water, the DIC increases from 1684µmol/kg to 2181µmol/kg. From 200 meters down to 2000 meters, the DIC increases to 2428µmol/kg in the open and coastal transects. For the Baja transect deeper than 200 meters, the DIC increases 129µmol/kg with depth.

In Figure 3b, the DIC and O_2 data are inversely proportional for the Baja and open water transects with an increase of nearly 2µmol/kg DIC per each µmol/kg of O_2 lost. For the coastal section, the DIC remains near the same concentrations (from 2146-2406µmol/kg) throughout the decrease of O_2 from 96µmol/kg down to 0.79µmol/kg.

NO_3^- increases from 0-46µmol/kg as the DIC increases from 1684-2428µmol/kg (Figure 3c). The coastal transect of water has the highest concentrations of both DIC and NO_3^-. The coastal waters do not have any DIC concentrations less than 2146µmol/kg and no NO_3^- concentrations less than 13µmol/kg.

DISCUSSION

In general, the pH of the water column changes significantly as the water gets deeper from 0-100 meters. This is due to the respiration which is simultaneously decreasing the O_2, indicated in Figure 2b as formula 1. Below 100 meters, the pH does not change at the same rate as the surface 100 meters. This is indicated in Figure 2b as formula 2. Therefore, these two formulas indicate that there is a significant difference between respiration at the surface water down to 100 meters and the respiration taking place throughout the rest of the water column. The concentration of phytoplankton growing at the surface produce organic matter which then degrades as it sinks through the water column. Deeper waters have gradually less organic matter due to the presence denitrifying bacteria consuming it and therefore there will be less respiration and a slower decline in pH.

The typical shape of a declining pH with depth curve would be a perfect logarithmic decay with depth. This data does not follow such a curve due to the abrupt shift at about 100 meters. In general, 100 meters is close to the oxygen minimum depth. Therefore, the shift in the curve corresponds to where the respiration changes from oxygen to nitrate as the electron acceptor. The change in the decay curve also indicates that respiration from nitrate is different than respiration from oxygen (Van Mooy, 2002).

When the pH changes are converted to DIC a clear picture emerges. The DIC changes with depth (Figure 3a) are more uniform across the ETNP relative to pH shown in Figure 2a. This trend is due to the increased sensitivity of pH as an indicator of respiration in relation to DIC. The changes we are able to detect in pH vary over a small and easily detectable range (6.5-8.1) compared to smaller variations of 100 units or less out of 2300 µmol/kg in DIC. When measured DIC changes in pH and alkalinity, a very small change in DIC has a large change in pH (Andersen, 2002).

The change in DIC as a function of O_2 reveals a relationship between inorganic carbon production and the various waters in the ETNP. The surface waters where there is O_2 consumption have a consistent DIC:O_2 relationship of 1.0. This is slightly higher than the value of 0.8-0.9 expected for the oxygenated degradation of organic matter (Anderson, 1994). One possible explanation for this is that the precision in measuring DIC was not high enough to accurately calculate a slope lower than 1.0. Nonetheless, these data show trends consistent with observations in other parts of the ocean (Andersen, 2002).

Once there was no O_2 remaining in the water column, the DIC continued to increase by about 150µmol/kg. This is the amount of DIC produced within the denitrifying oxygen minimum zone. This is much more DIC production than can be accounted for simply assuming a 1:1 with a nitrate deficit (Macmillan, 2012) which is about 25µmol. One possible explanation for this is that the sinking particulate organic matter contains nitrogen which was not reflected in the nitrogen budget but can fuel respiration and DIC production (Gruber, 1997).

The third part of the graph illustrates increasing O2 concentrations with little change in DIC. This is a result of bringing in oxygenated Antarctic intermediate water. The DIC does not decrease because the pressure at those depths allows for more DIC to stay in solution because it is deeper than the carbonate compensation depth.

In oxygenated waters, a plot of dissolved inorganic carbon and nitrate should show both of them increasing because respiration and nitrification should both be happening. Once the O_2 is consumed, the relationship between DIC and NO_3^- should change due to the onset of denitrification, causing DIC to increase and NO_3^- to decrease. The upwelling Antarctic intermediate water which contains more NO_3^- comes into this region with a higher NO_3^-:DIC ratio (Figure 3c).

OCEAN ACIDIFICATION

The oceans are becoming more acidified due to the increasing concentrations of CO_2 in the atmosphere that are then being absorbed into the ocean basins, forming (H_2CO_3) and lowering the pH of the water column. The pH for the same latitude within the sub-tropical Pacific Ocean was predicted to be at about 0.06 units less at a water depth between 100 to 250 meters (Byrne, 2010). The water column from the surface down to approximately 500 meters is theorized to be acidifying (Byrne, 2010). At approximately 250 meters, the pH should be at about 7.8 based on the data presented within the paper published by Byrne from data collected in 2006. The data collected in the ETNP reflect a pH between 7.3-7.6 at a similar depth range, showing this water has undergone more acidification than water at the same latitude to the west. Part of the change in pH from the central Pacific samples and the samples collected in the ETNP is due to the anoxic nature of the water. The relationship between O_2 and pH along the Baja peninsula, where the O_2 concentration never goes to zero, can be calculated to find the correction value for the Byrne estimate of 7.8 to account for the 'missing' O_2 using the equation: $y= 355(pH)-2641$, with an $R^2= 0.89$. Thus, I predict that the pH at 250 meters' depth should be at about 7.52. For all of the samples I collected south of Baja, the pH is lower than that value (Figure 2a), indicating that there is ocean acidification taking place in this region.

The location of the stations where ocean acidification was evident directly correlates to the location of the most widespread anoxic pool in the region (Carl, 2012). This anoxic pool affects the ecosystem in potentially negative ways. Any marine organisms that need to utilize carbonate ions in order to live could be destroyed as a result of the lowered oceanic pH.

Given the data at hand, I cannot definitively say whether this acidification is due to natural or anthropogenic causes. One way to differentiate between the two potential explanations for the acidified water column would be to conduct this research more frequently with more sampling locations in and around the region to compare the water column changes from outside and within the anoxic zone. Another way of measuring the differences between anthropogenic CO_2 influx and the natural expansion of the anoxic zone would be to conduct measurements of the CO_2 within the region to look at how much is actually being added to the area.

Continuous data collection in the ETNP and surrounding areas can be done using buoys and autonomous systems. The national oceanographic and atmospheric administration—NOAA—Pacific marine environmental laboratory—PMEL—has buoys stationed throughout the Pacific Ocean to measure the partial pressure of CO_2 (pCO_2) in the surface water. These moorings, buoys, and even some underway systems with pCO_2 sensors will be joined by pH, oxygen, chlorophyll, and turbidity sensors to help better identify the environmental changes associated with ocean acidification (PMEL's carbon group). Currently, PMEL does not have a data collection network in or near the ETNP.

CONCLUSIONS

- In oceanic upwelling zones like the coast of Mexico near Manzanillo, where there is very low oxygen, ocean acidification is likely to be present.
- Due to the location of this ocean acidification, there are implications that the near shore intertidal ecosystem will be negatively affected due to the large percentage of calcium carbonate ($CaCO_3$) shelled organisms reside in that ecosystem (clams, urchins, sea stars, barnacles, coccolithophores, etc.).
- The eastern tropical north pacific OMZ is expanding to deeper and shallower water since 1972 when Kline and Richards conducted their research in the region, increasing the area affected by ocean acidification. This region needs to be studied more in depth over a longer period of time in order to more accurately determine the effects of ocean acidification.

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Mettler-Toledo accuracy readings
http://si.mt.com/dam/mt_ext_files/Editorial/Generic/4/ChemicalsNews03_0405_Editorial-Generic_1207571456457_files/chemicalsnews3_en4-51207571456457.pdf

APPENDIX

Standard pH	**4.0**	**7.0**	**10.0**
	3.879	6.853	9.743
	3.878	6.856	9.741
	3.888	6.857	9.745
	3.885	6.86	9.743
	3.89	6.863	9.745
	3.899	6.864	9.747
	3.893	6.864	9.749
	3.904	6.865	9.729
	3.891	6.866	9.746
	3.905	6.871	9.744
Average pH	3.8912	6.8619	9.7432
Variance	0.1088	0.1381	0.2568
pH adjustment			0.1679

Appendix 1: pH sensor standardization data