2013

Casco Bay Clam Flat pH Study, 2013

Friends of Casco Bay

Friends of Casco Bay
Casco BAYKEEPER®

2013 Casco Bay Clam Flat pH Study

June 30, 2014

Introduction

The pH of the world's oceans has decreased by 0.1 over the past 150 years, representing a 30% increase in acidity. Globally, ocean acidification is caused by increasing concentrations of atmospheric carbon dioxide reacting with the water to form carbonic acid, increasing acidity and lowering pH. However, close to shore, coastal acidification is also occurring as a result of nitrogen pollution, which promotes algal blooms in excess of what would occur naturally. When these algae die and decompose, excess carbon dioxide is released into the water and sediments. Local coastal acidification is an issue in Casco Bay, reducing the productivity of clam flats and making the Bay more susceptible to ocean acidification. Increasing acidification lowers the availability of carbonate ions in water and sediments, and can impair the ability of calcium carbonate-bearing organisms, such as the soft-shell clam *Mya arenaria*, to build and maintain their shells. Small bivalves, such as newly-settled clams, may dissolve completely. This process, termed "Death by Dissolution" is considered a leading cause of mortality in young clams (Green 2004, 2009).

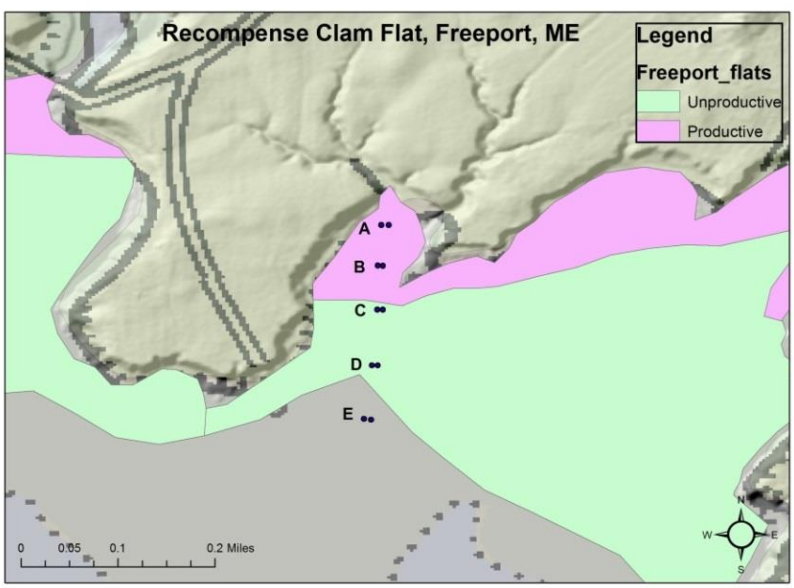
Project Description

There were two primary goals for this phase of Friends of Casco Bay's study of pH in mud flats. One goal was to measure spatial and temporal variability of sediment pH in a clamflat in Casco Bay. The other goal was to compare our in-situ pH measurements to pH values calculated from lab analysis of simultaneously collected sediment samples. The pH measurements were also compared to the calculated omega aragonite. We will look at the relationship between these parameters in order to address the robustness of in-situ pH as an indicator of mudflat acidity.

In-situ monitoring yields great benefits in comparison with traditional sampling because process information can be gathered in a short time at low cost. In addition, sources of error are avoided, for example selective sampling or disturbing chemical changes during transport. Real-time in-situ measurements can also be used for screening purposes, for example selection of a clamflat with the lowest sediment pH or the best time of year to deploy clam spat.

Site Description

Recompence clamflat, located near the Wolf Neck Farm Campground in Freeport, Maine, was the location of this study. Two transects, with five stations each, were set from the head of the cove to the low tide mark. The two transects are roughly 10 meters apart, with about 90 meters between each station.



Due to the length of the mud flat, the first station is exposed about 3 hours prior to low tide and the last station is exposed just prior to low tide. This study site was chosen due to the gradual slope of the flat, and to the fact that clam productivity had dropped significantly within recent years in the outer half of the flat. Each station was marked with a wooden stake. Station A and B are in the upper reaches of the flat, and are still considered productive, while stations C and D are in the lower, unproductive region of the flat. Station E was located just along the edge of a historic clam habitat, bordering an eelgrass bed. The productive and unproductive classifications were provided by the Town of Freeport.

Summary of Method

In 2013, monitoring took place twice a month in June, July and August, and once in September. Prior to any monitoring event, the pH meter and electrode were calibrated to 3 points at pH 7.01, 4.0 and 10.0. The clam flat was monitored on an outgoing tide, at about 3 hours before the day's low tide. At each monitoring event, the water pH, salinity and temperature were measured between the second and third sediment measurement stations. Within a few inches of the waterline, following the outgoing tide, 10 measurements each of pH and temperature were collected from the top 5 millimeters (less than 1/4 inch) of sediment, in an area no larger than 1 foot square. Three oxidation-reduction potential (ORP) measurements were collected just after pH measurements #2, #5 and #9. After the first five measurements at each station, the electrode was cleaned and calibrated to three points at pH 7.01, pH 4.0 and pH 10.0. After all 10 measurements were completed; a straight edge was used to pull the top 5 millimeters of sediment from the 1 foot square measurement area into a small pile, from which all samples were collected. Sediment samples were collected with a plastic spoon and placed into two 50 mL centrifuge tubes, filling the tubes completely and leaving no head space. These samples were analyzed for dissolved inorganic carbon (DIC) and titration alkalinity (TA). Immediately, all samples were placed on ice in a cooler, and then delivered to the appropriate lab at the conclusion of the sampling event.

A critical component of this work was the care and maintenance of the pH electrode. The electrode solution was topped off prior to every monitoring event, and replaced completely after every four events.

The sediment pH, sediment temperature, and sediment ORP values were determined directly from meter readings. The water pH and temperature values were also determined directly from meter readings. Water salinity was measured with a hand-held refractometer. Samples were prepped, and the TA of the sample was determined at Resource Access International LLC, in Brunswick by Darcie Couture. TA was measured using 5 mL pore water samples after the method of Edmond (1970). From there, samples were delivered to the University of New Hampshire for analysis of DIC by Dr. Joe Salisbury. DIC was measured using an automatic DIC analyzer on 10 mL samples. The program CO2SYS allowed estimates of omega aragonite using values of DIC and TA, salinity, temperature, and the first and second dissociation constants for CO_2 in seawater after Roy et al. (1993). Calculated pH values were estimated using DIC and TA by Mark Green of St. Joseph's College.

Results and Discussion

Clam flat pH temporal trends

There was a significant dip in sediment pH values during the summer months. Average pH values of over 7.4 in early June dropped to 7.12 in late June, and then from 6.96 through 6.80 in July, before hitting the lowest mean values of 6.80 in early August. However, values climbed to near spring levels in late summer and early fall, returning to 7.19 by late August and then 7.39 in September. This difference in pH over time suggests that future comparisons of measurements made among flats need to take into account variability due to seasonality (Figures 1 and 2).

Figure 1. Bivariate Fit of Average pH By Date

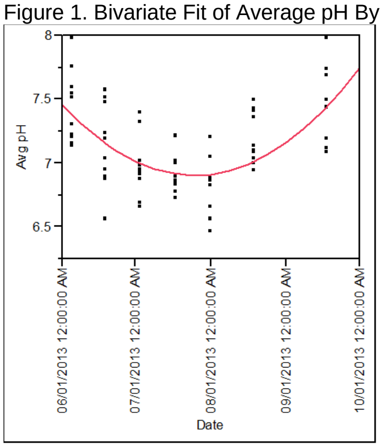
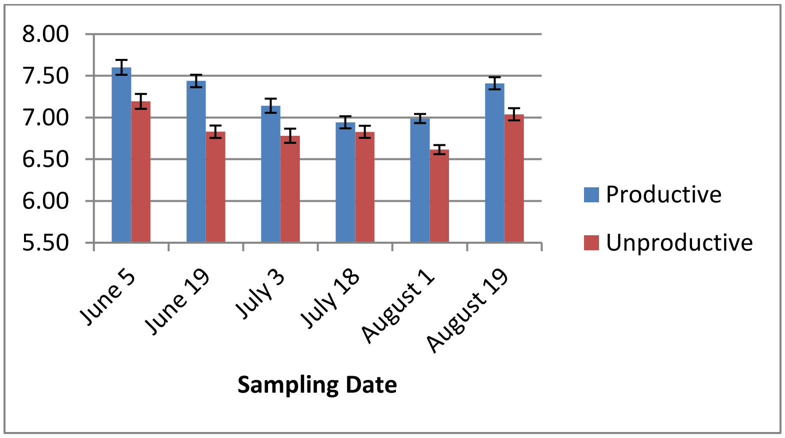


Figure 2. The seasonal differences in pH were evident when comparing the mean pH values of the Productive and Unproductive sites over time.



Clam flat pH spatial trends

Sediment pH values were generally higher at the upper two stations, Stations A and B, and lower at the two unproductive stations, C and D, resulting in a significant difference between mean values of the two categories (Figure 4). The Productive clam flat stations had a higher sediment pH than the Unproductive stations. Mean sediment pH at station E was slightly higher than stations C and D, but still well below the levels found at stations A and B (Figure 3).

Figure 3. Oneway Analysis of Average pH By Station

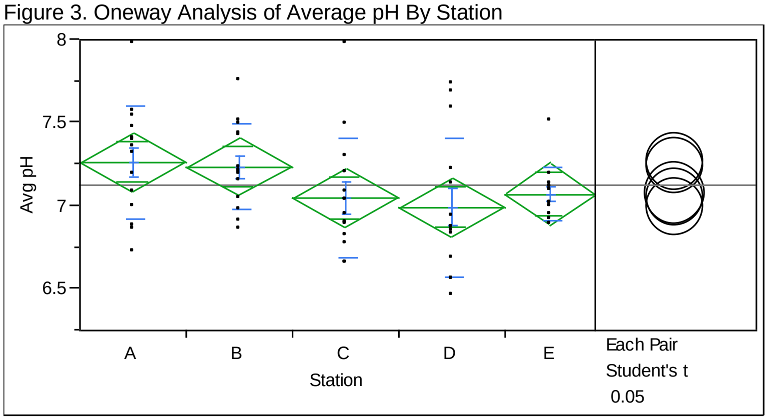
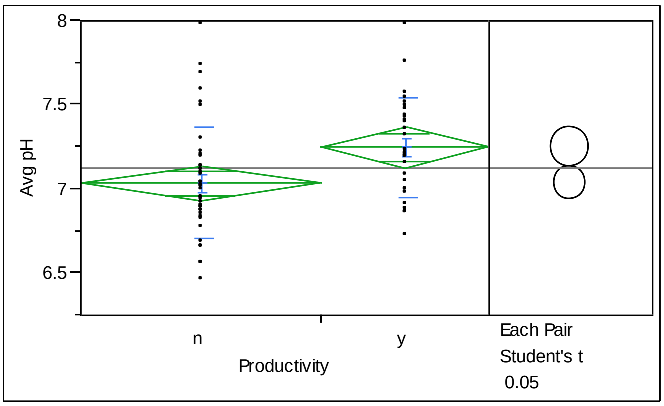
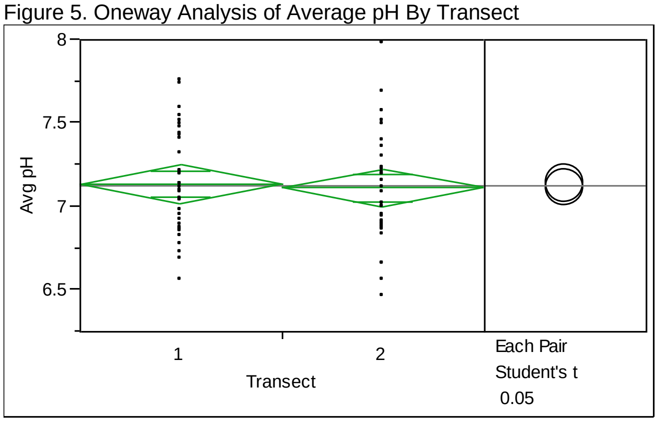


Figure 4. Oneway Analysis of Average pH By Productivity. The “n” indicates Unproductive stations, and “y” indicates Productive.



There was general agreement in mean pH between the two transects, with much of the variability due to seasonal differences (Figure 5).

Figure 5. Oneway Analysis of Average pH By Transect

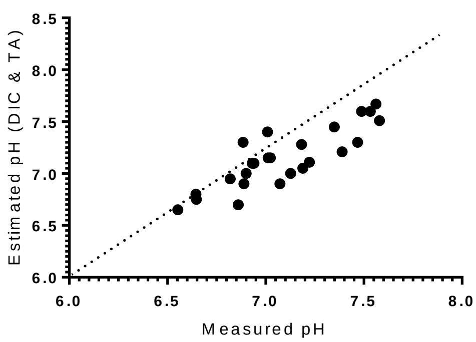


Calculation of pH and omega aragonite versus in situ measurements

If we consider the laboratory-based analyses to provide the more accurately determined pH values, our in-situ pH measurements correlated very well, but were generally slightly lower, as seen in Figure 6.

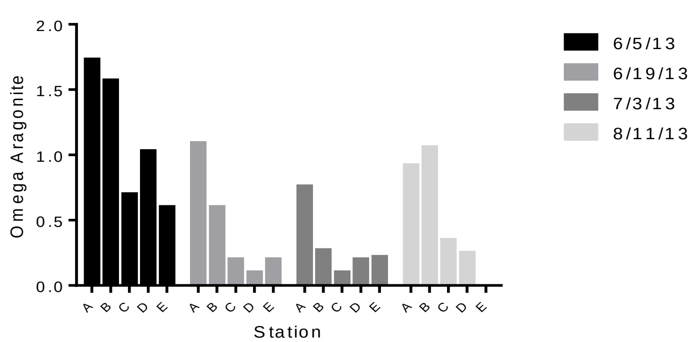
Therefore, use of a pH electrode (assuming the proper protocol is used) can provide valuable information about the overall acidity of the mud. This demonstrates that our sediment pH protocol can be considered a viable proxy for the more expensive and time-consuming laboratory analysis.

Figure 6. In-Situ pH measurements by direct electrode insertion into surface mud compared to pH estimated from DIC and TA. The hashed line is the 1:1 relationship.



As we moved down the flat, seaward, in situ pH decreased. Correspondingly, omega aragonite values also decreased from shore, seaward, as seen in Figure 7.

Figure 7. Omega aragonite values at stations A-E.



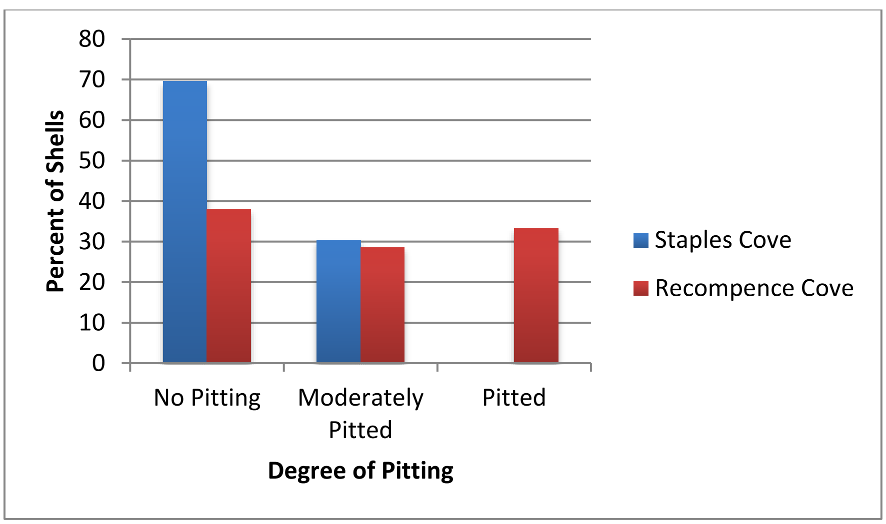
Spat deployment

Hatchery-reared *Mya arenaria* spat were deployed in the sediment at Recompence flat and at a reference flat (Staples Cove) for 19 days during the fall of 2013. These 4-5 mm clams were exposed to sediment with higher pH (around 8.0) at the reference flat and lower pH (below 7.5) at Recompence. The goal of this effort was to determine if shell dissolution was occurring in Casco Bay, and to compare differences in shell condition between a low pH environment and a high pH environment. At each of these coves, 2 sets of 10 spat were placed near the middle of the flat, with each group approximately 1 foot apart. The samples were deposited in a 2-inch-wide, 6-inch-long PVC pipe with a square of 1 mm rubber window mesh secured around the top with an elastic band. The pipes were gently pressed around each set of spat until the top of the PVC pipe was flush with the mud. The PVC pipes were scooped out of the flat by hand after 19 days of treatment and delivered to the lab on ice. All spat were quickly removed from the soil using a 1 mm sieve and were left in sample tubes overnight to dry. The *M. arenaria* shells were treated with a 1% hydrogen peroxide solution to remove excess organics, rinsed with purified water, and soaked in a 99% EtOH solution for 3 minutes before a final rinse with purified water. The spat were photographed at 10x magnification and evaluated for degree of shell pitting. Shell with obvious signs of dissolution were later photographed with a scanning electron microscope at Bowdoin College.

As previously noted, during the fall, mean pH values increase from the lower values measured during the summer. For this reason, and because the spat were relatively larger than others used previously in similar lab studies, we did not expect to see extensive damage to shell material or any difference between sites.

However, after 19 days there was considerable damage seen in the Recompence spat and very little dissolution evident in the Staples spat (Figure 8.).

Figure 8. Differences in Degree of Shell Pitting between High pH (Recompence) and low pH (Staples).

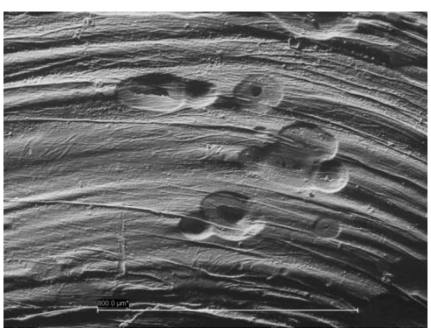


Examples of images from this study are seen in Figures 9, 10 and 11. Figure 9 shows a healthy clam after exposure to the high pH environment in the reference flat at Staples Cove. Figure 10 shows a pitted clam from the low pH sediment at Recompence flat, and Figure 11 is a scanning electron microscope image of the same Recompence clam to show a close-up of the pitting.

Figure 9. Example of a clam from sediment with high pH (Staples Cove).

Figure 10. Example of a clam from sediment with low pH (Recompence flat).

Figure 11. Close-up of the same clam seen in Figure 10. The scale bar at the bottom of the image is 800 um.



Conclusions

The 2013 Friends of Casco Bay Clam Flat pH study was successful in documenting that coastal acidification is occurring in local clam flats, and that the pH measurement protocol used in the study is effective in assessing the acidity of the sediment in the clam flats.

Appendix A.

A List of Presentations that Reference the 2013 Clam Flat pH Study:

Nov, 21, 2013, Falmouth, ME, Falmouth Library OA discussion, 18 people

Jan 16, 2014 Augusta, ME, Maine OA meeting, 100+ people

March 21, 2014 Stamford, CT, Nestle Waters North America, 50 people and television coverage

June 12, 2014, Maine Calling interview on OA, MPBN radio

June 19, 2014 Yarmouth, Royal River Conservation Trust 45 people

Friends of Casco Bay is deeply appreciative of the generosity of the funders for this work:

Bowdoin College McKeen Center for the Common Good, Casco Bay Estuary Partnership, The Robert and Dorothy Goldberg Charitable Foundation, the Town of Harpswell, Horizon Foundation, Patagonia, Quimby Family Foundation, and the John Sage Foundation.