Expanding the Reach of Coastal Carbon Cycle Observations: Through Organic Alkalinity Characterization and Utilization of Predictive Carbon-System Algorithms

Nina Buzby, Middlebury College & San Francisco Estuary Institute

Mentor: Andrea Fassbender

Summer 2018

Keywords: Organic alkalinity, carbon cycle, coastal observations, ocean acidification

ABSTRACT

This work contributes to add to efforts to fully and accurately characterize the local Monterey Bay carbonate system, by first assessing West Coast and Monterey Bay regions for organic alkalinity influence and then using predictive algorithms. Both literature-based algorithms and a developed region-specific MLR were utilized. Findings from organic alkalinity analysis of NOAA West Coast Ocean Acidification cruise data showed no significant influence, while results from a filtered subset of MBARI Biological Oceanography Group (BOG) data were less conclusive. The small dataset combined with evidence of organic alkalinity influence in the near shore Elkhorn Slough environment, motivates further analysis of future discrete measurements in the bay. Of four pre-existing algorithms, two produced reasonable RMSE values when applied to data from in the Monterey bay system. These algorithms were LIAR/LIPHR and CANYON. They preformed best on data from 2018, which coincided with the start of sample analysis at MBARI facilities. The development of a region-specific algorithm elucidated data variance within the BOG dataset most likely caused by a 2012-2014 climatic phenomenon known as the Blob. Applying all algorithms to a unique set of glider data (Rudnik, 2017), showed the potential for high-resolution carbonate system depictions. Although, further quantitative validation of this application is recommended, given the unavailability of 2017 CalCOFI data.

INTRODUCTION

There is growing evidence of ocean acidification observations in the open ocean, however detecting similar pH declines in coastal zones proves more difficult. In coastal environments, various natural and anthropogenic processes can alter the carbonate chemistry and lead to a greater variability in pH (Waldbusser and Salisbury 2014; Takeshita et al. 2015). Coupling this unpredictability with the intrinsic complexities of the carbonate system underlines the importance of fully constraining such coastal biogeochemical cycles.

The carbonate system is commonly described through four principal components: dissolved inorganic carbon (DIC), pH, partial pressure of carbon dioxide, and total alkalinity (TA). The interrelationships between these parameters are advantageous in the context of carbon system characterization. Measurements of any two parameters – along with temperature, pressure, and salinity – allow for the calculation of all other carbonate system components (Dickson et. al., 2007). However, all four parameters have aspects that make them difficult to measure and/or constrain. For example pH and DIC vary with salinity and temperature, while pCO_2 can be greatly influenced by the air-sea CO_2 exchange.

TA is described as an "unconstrained" parameter, meaning it does not vary with temperature or salinity and thus appealing for use in carbonate calculation. TA in marine and estuarine waters is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors within the system (Hernandez-Ayon et al., 2007):

$$\text{T-Alk} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3PO_4] + [SiO(OH)_3^-]$$

Generally carbonate, borate, and nutrient-related species are the main contributors to total alkalinity, and contributions from organic species are assumed to be negligible (Kim, Lee, & Choi, 2006; Hernandez-Ayon et al., 2007). However, studies have shown that organic alkalinity is sometimes a significant fraction of total alkalinity in estuarine and coastal waters (Cai et al., 1998; Bradshaw & Brewer, 1988; Kim, Lee, & Choi, 2006; Hunt, Salisbury & Vandermark, 2011). Possible sources of contributing bases include humic materials, phytoplankton exudates, bacterial cells, microalgae, as well as dissolved and suspended organic matter (Cai et al., 1998; Hernandez-Ayon et al., 2007; Kim, Lee, & Choi, 2006; Yang, Byrne, Lindemuth, 2015; Kulinski et al., 2014). The addition of such weak organic bases to seawater leads to a shift in the contributions of inorganic species and can also increase total alkalinity (Kulinski et al., 2014). Examples of organic alkalinity offsets and resulting miscalculations can vary based on the watershed, the greatest of which was reported in the Baltic Sea. This work showed a 1.5-3% organic alkalinity contribution lead to a 27-56% offset in pCO_2 values and 0.4 difference in calculated pH (Kulinski et al., 2014).

Therefore, assessing coastal environments for organic alkalinity influence allows for a more accurate representation of the local carbonate system. This is particularly important in relation to algorithm development efforts that aim to predict carbonate parameters from more ubiquitous biogeochemical properties. Shipboard measurements of are often isolated and sparse, and autonomous float sensors – though growing in location and number – can only currently measure one of two carbonate parameters required to constrain to system (Fassbender et al., 2016; Carter et al., 2016). Both these sources lack the information needed for comprehensive carbonate system characterization, and motivate the development of predictive algorithms. However, these predictions can short, given intrinsic inaccuracies like organic alkalinity influence.

This work begins to fully and accurately characterize the local Monterey Bay carbonate system. The first step of these efforts assessed West Coast and Monterey Bay regions for organic alkalinity influence. The following stage, focused on utilizing literature-based algorithms as well as developing a Multiple Linear Regression approach specific to the Monterey Bay Region. This order of investigation lead to a thorough and enhanced understanding of the local carbonate system.

METHODS

Organic Alkalinity Analysis

Utilizing a progressively narrowed spatial approach, organic alkalinity influence was first assessed along the entire West Coast of the U.S. and then constrained to the Monterey Bay region as well as near shore Elkhorn Slough. Datasets for this assessment came from NOAA West Coast Ocean Acidification (WCOA) cruises and the MBARI Biological Oceanography Group (BOG). The NOAA WCOA dataset included data from three viable cruises from 2011, 2013, and 2016. The BOG dataset includes monthly cruises dating back to 2011, however this study only focused on data from December 2017 to July 2018 as this period contained spectrophotometric pH values compared to previous glass-electrode pH measurements. Additionally, the more recent BOG dataset did not yet have associated silicate and nitrate concentrations. Average nutrient concentrations, by depth, from the previous six years were used as proxy values for these variables. July 2018 BOG spectrophotometric pH data was run on two systems – lab and ship-based – to compare instrument performance as well as any data variation due to sample poisoning. The in-lab system used an Agilent 8453 diode array spectrophotometer, while ship-based analysis was run on a Mini MMS.

Eleven discrete samples from Elkhorn Slough were collected at morning high tide from May-July 2018 at two stations located at the mouth of the Salinas River – L01, and further back in Elkhorn Slough – L03 (Figure 1). Coinciding CTD casts also occurred during each sampling event in Elkhorn Slough. Each water sample was filtered prior to analysis. Filtering times varied, however samples from L03 sat for at least an additional 24 hours compared to L01 stations, given the higher level of suspended particles in the Slough samples. Carbonate system parameters were analyzed using the same instrumentation as the BOG monitoring cruise data.

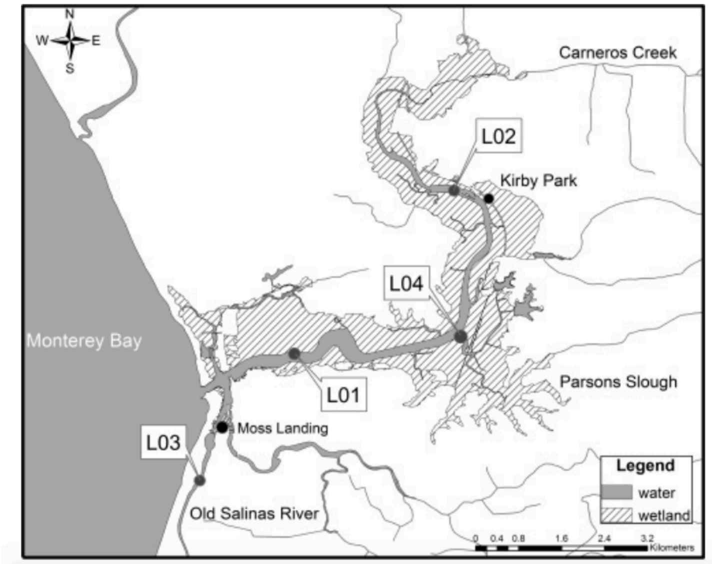


Figure 1. Map of Elkhorn Slough, CA moorings that coincide with the to discrete sampling locations at L01 and L03. (Johnson et al., 2007)

Calculated total alkalinity was found using the CO2SYS for MATLAB routine by van Hueven et al. (2011) and then compared to discrete measurements. Organic alkalinity significance was then determined given a 95% confidence interval of both CO2SYS calculation errors (James Orr) and discrete measurement uncertainty (Table 1). Given the greater distance from shore and broader depth profile, median alkalinity at each station was additionally determined for NOAA WCOA data.

Table 1. Reported error associated with CO2SYS input parameters for use in error propagation calculations to determine significant organic alkalinity

Input Parameter	Reported Error	Source
Salinity	0.002 PSS-78	NOAA WCOA Metadata
Temperature	0.001ºC	NOAA WCOA Metadata
Pressure	1 dbar	NOAA WCOA Metadata
Silicon	1 umol/kg	NOAA WCOA Metadata
Phosphate	0.02 umol/kg	NOAA WCOA Metadata
TA	0.1%	Empirically determined[+]
pH	0.01 (for values >7.8)	Carter et al., 2017
DIC	0.1%	Empirically determined[+]

Algorithm Testing and Development

Four literature-based algorithms were assessed for applicability to the Monterey Bay region (Table 2). Each algorithm was compared against both the NOAA WCOA and BOG datasets for

[+] Five error scenarios were tested to determine how many remaining measurements would be viable for organic alkalinity analysis. These error values were determined to be sufficiently conservative, while not over-eliminating data points.

applicability, by assessing closeness between actual and calculated values for associated carbonate system parameters.

Table 2. Literature-based algorithms references and methods. Parameter abbreviations are as follows; T-temperature, S-salinity, O-oxygen, P-pressure, θ-potential temperature, NO_3—nitrate, Si-silicate

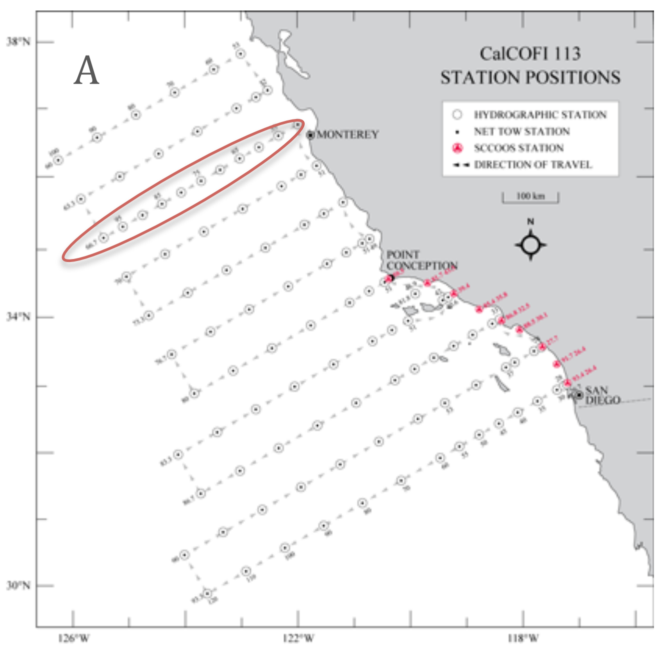
Algorithm Name	Method	Source	Geographic Region & Training Dataset	Parameters	
				Input	Output
Gray	Linear	Gray et al., 2011	Monterey Bay, CA	S	TA
Alin	MLR	Alin et al., 2012	Southern CA	T, S, O	pH, Ω_{Ar}, Ω_{Ca}, TA, DIC, Carbonate
LIAR, LINR, LIPHR	MLR	Carter et al., 2017	Global, GLODAP	T, S, O, θ, NO_3^-, Si	TA, pH, NO_3^-
CANYON	Neural Network	Sauzéde et al., 2016	Global, GLODAP	Lat, Lon, Date, P, T, S, O	TA, pH, pCO_2, NO_3^-, PO_4^{3-}

A Monterey Bay region-specific, multiple linear regression (MLR)-based algorithm was also developed using a fit regression model. Multiple combinations of variables (temperature, salinity, oxygen, NO_3^-, pressure, density, and potential density) were tested using stepwise regressions to determined the strongest predictive variables for estimating pH, TA, DIC, and [NO_3^-] (similar to methods in Carter et al., 2017 and Alin et al., 2012). The calibration data for this algorithm development came from monthly BOG cruises from 2011 through July of 2018. The training versus validation split of data was 75% to 25%, respectively.

Predictive input variables were determined based on those used in the literature, as well as what measurements would hypothetically be taken on coastal profiling floats if/when deployed in the future. All independent variables were tested for collinearity using pairwise regression and a variance inflation factor test (VIF) with an upper cutoff value of 5. Variables deemed collinear were eliminated. A robust linear regression was used (designed to overcome limitations of traditional parametric and non-parametric methods) to determine the ultimate set of predictive variables as well as the final resulting RMSE values.

An application of this region-specific developed algorithm was tested using a selection of autonomous glider data taken along line CalCOFI station line 66 (Figures 2) during the spring and summer of 2017 (David Rudnik, 2017). Measurements of temperature, salinity, oxygen, and pressure from the glider data were used as input variables to generate predictive contour plots of various carbonate parameters such as TA and aragonite saturation state (Ω_{Ar}).

Initial validation of this application was accomplished by plotting discrete data measurements taken from the NOAA WCOA 2016 cruise data overtop the produced contour plots. This was purely a qualitative approach given that the year and geographic location of the data sources did not coincide (Figure 3). Results were then assessed through a visual comparison of contour colors.



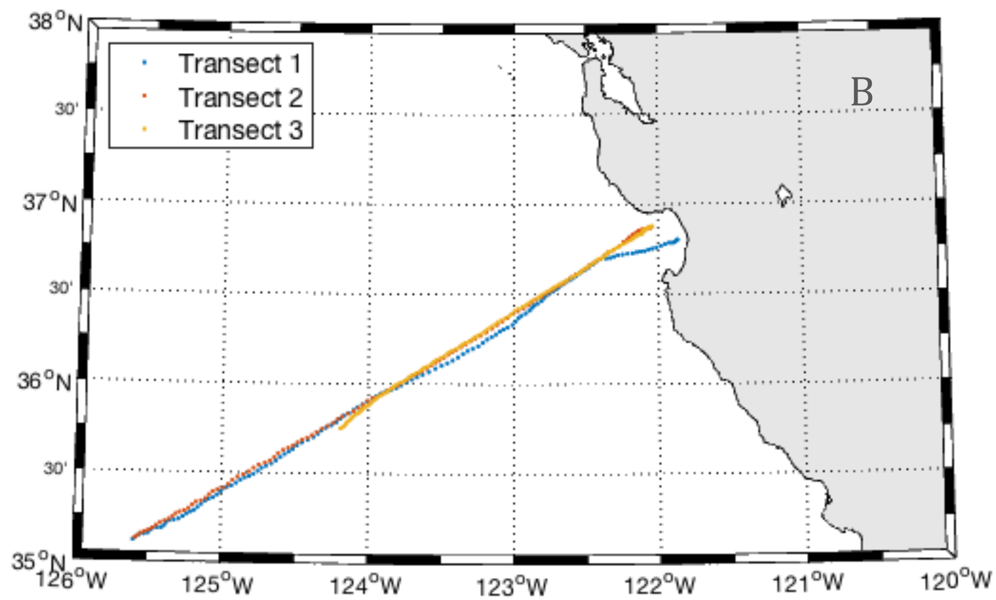
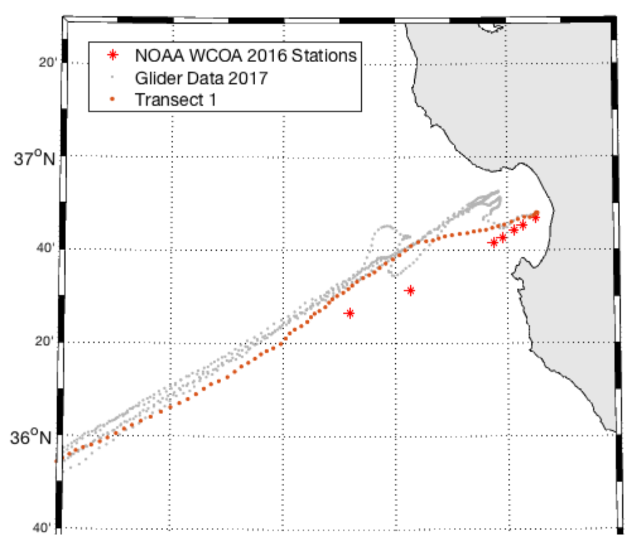


Figure 2. (A) California Cooperative Oceanic Fisheries Investigations (CalCOFI) sample pattern outlining sampling stations. Red ellipse indicates location of line 66 and the basic trajectory of the glider. (B) Location and trajectories of selected glider transects.



RESULTS & DISCUSSION

Organic Alkalinity

<u>1. NOAA West Coast Ocean Acidification (NOAA WCOA) Cruises</u>
Adhering to rather conservative uncertainties related to pH, total alkalinity, and DIC measurements as well as a 95% confidence interval, less than 10 stations per cruise year showed evidence of statistically significant organic alkalinity presence (Figure 4). These stations were also located close to one another, and generally showed median organic alkalinity values less than 5 umol/kg. These low median values as well as geographic clustering indicate that what could be proposed as "organic alkalinity" input, is more likely a result of instrument or analyst error.

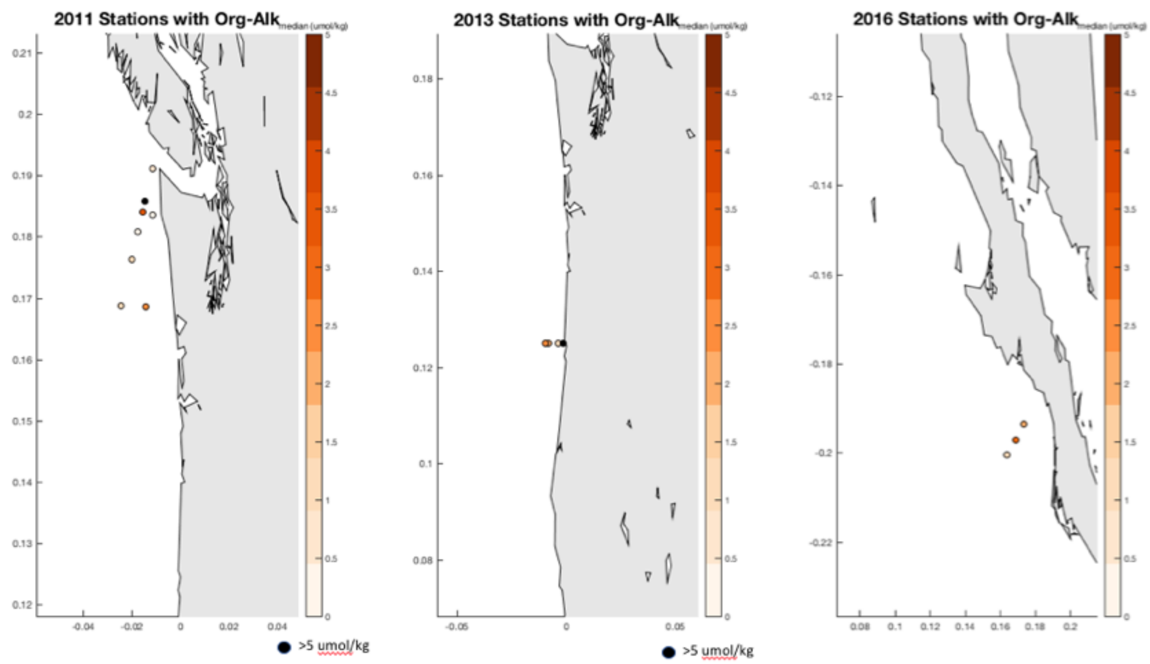


Figure 4. Mapped locations of significant organic alkalinity stations from three years of NOAA WCOA cruise data. Coloring of each circle indicates the median organic alkalinity input per station; black circles indicate stations with greater than 5 umol/kg influence.

However, it is notable that significant station locations somewhat coincided with the starting locations of each cruise (ie. Baja California – 2016 start local in San Diego, CA; OR coast – 2013 leg2 start local in Newport, OR). The 2011 cruise, which showed the highest median organic alkalinity values, also occurred following a period of peak Columbia River discharge, in June-July of that year (Figure 5). This high flow could explain the more numerous and spread out nature of the significant organic alkalinity data associated with the 2011 cruise.

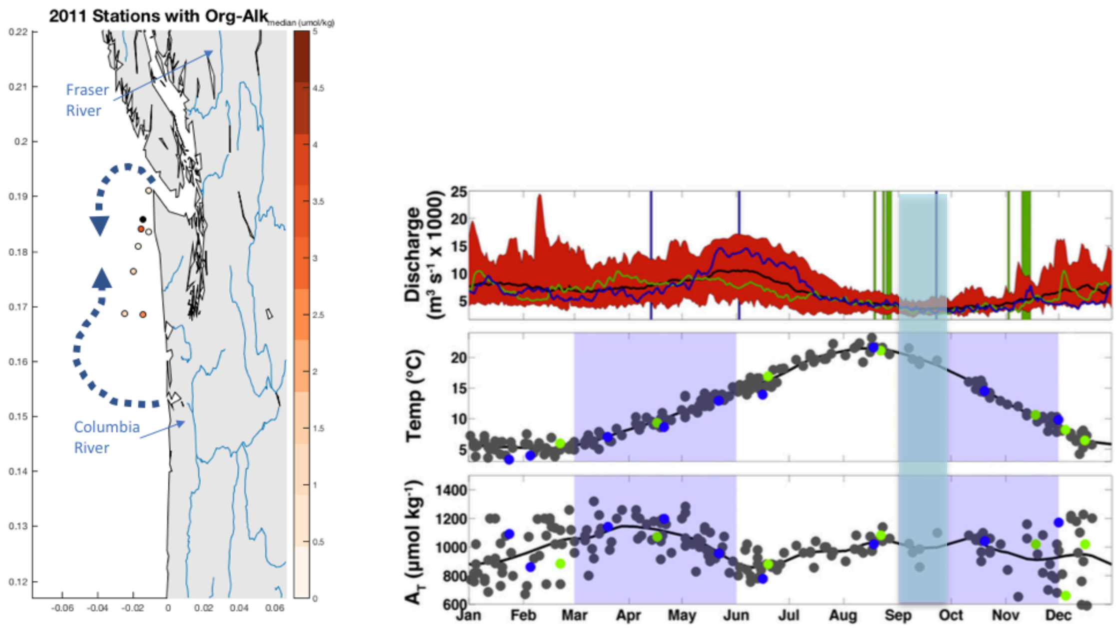


Figure 5. (A) Location and flow of two major rivers along the coast of Western Washington, relative to NOAA WCOA 2011 significant organic alkalinity stations. (B) Sourced from Evans et al., 2013; Columbia River discharge in 2011. Teal shaded rectangle indicates timing of the 2011 WCOA cruise.

<u>2. Biological Oceanography Group Cruises – Monterey Bay</u>

Resulting organic alkalinity analysis in Monterey Bay showed six significantly influenced data points from the BOG 2017-2018 limited dataset (Figure 6). The most significantly influenced samples were all located in the same station within Monterey Bay [M01] and came from the same cruise [BOG 34017]. This trend most likely indicates a lack of significant organic alkalinity presence in the Bay and instead a reflection of an isolated instance of instrument and/or user error. It should be noted that the concentration of organic alkalinity generally tends to decrease with distance from shore and with depth.

However, these findings are not entirely conclusive. The data points only span a period of 6 months and the nutrient concentration values used as input variables were average values, rather than actual in-situ measurements. Follow up organic alkalinity analysis using more and accurate input data would help elucidate the extent of the influence in Monterey Bay.

<u>3. Elkhorn Slough</u>

Similar to the BOG dataset, the samples taken from Elkhorn Slough were awaiting nutrient concentration measurements prior to conducting to organic alkalinity analysis. Therefore organic alkalinity influence cannot be fully characterized. However, previous studies confirm the influence of organic alkalinity in Elkhorn Slough (McLaughlin et al., 2017).

Results show indication of high organic alkalinity influence within the slough. All but one of the discrete samples at station L03 had statistically significant delta values when comparing measured and calculated alkalinity (Figure 7). Samples from L01 – located at the Salinas River (Figure 1) – lacked this significant difference likely due to the high flow and exchange with Bay waters experienced at the river mouth.

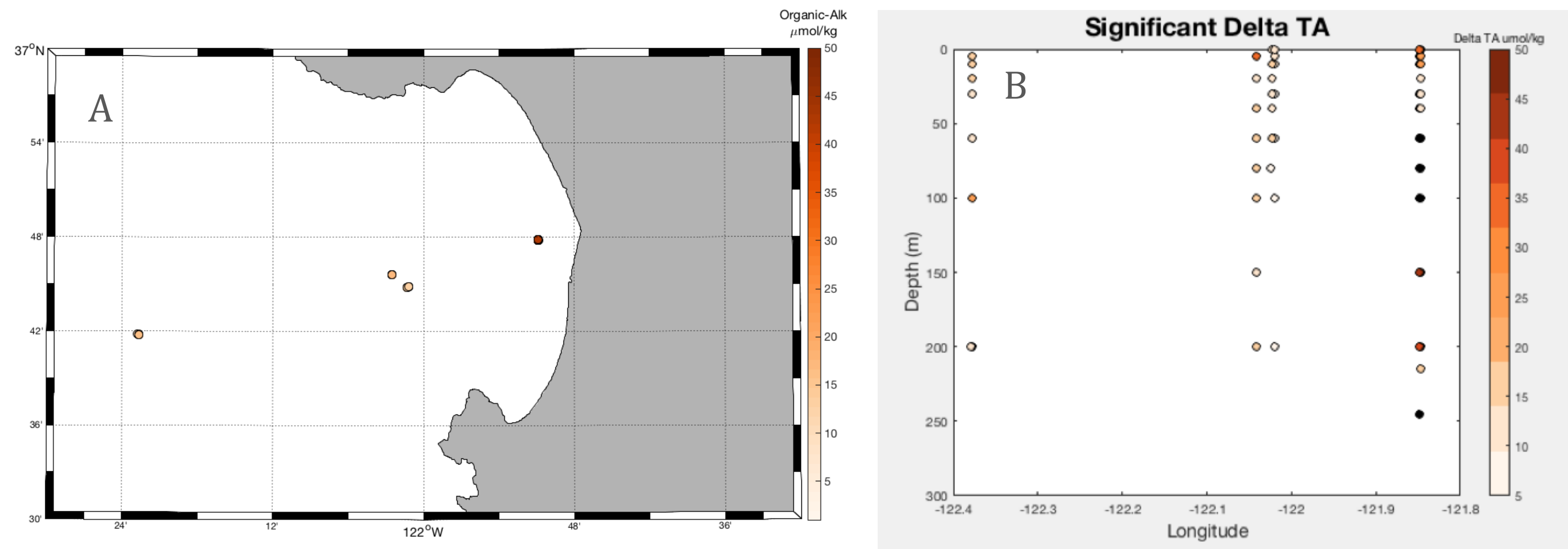
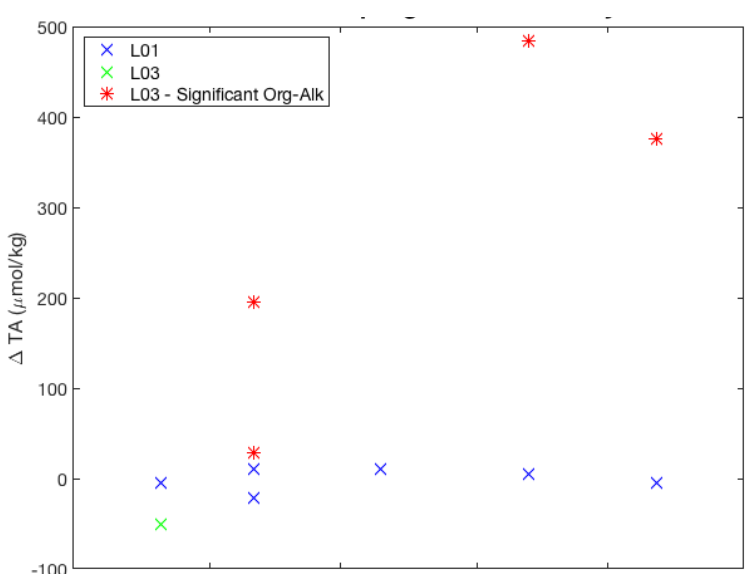


Figure 6. (A) Mapped locations and values of median organic alkalinity influence at stations from BOG dataset, (B) as well as associated depth profiles for these significant stations. Depth profiles show the difference between measured and calculated total alkalinity that indicate organic alkalinity influence – which are statistically significant – while the map shows actual organic alkalinity values in μmol/kg.



Algorithm Testing and Development

1. Literature Based Algorithms

Resulting RMSE values showed that pre-established algorithms predict TA and pH relatively well when applied to the NOAA WCOA dataset, while less so when applied to BOG data (Tables 3 & 4). For WCOA applications, the LIAR and LIPHR algorithms (Carter et al., 2017) had the lowest RMSE values across all years (Tables 3 & 4). It was found that LIPHR was particularly effective when used without the newly incorporated date-specific ocean acidification adjustment [Carter et al., 2017] (Table 4).

Table 3. Total Alkalinity estimation RMSE results for literature algorithms on NOAA WCOA cruise data and MBARI BOG data. Notably high and low values are highlighted in blue and orange, respectively.

BOG					**WCOA**				
Year	Algorithm				Year	Algorithm			
	Gray	**Alin**	**LIAR**	**CANYON**		**Gray**	**Alin**	**LIAR**	**CANYON**
2011	34.50	16.48	10.34	9.69	**2011**	16.64	25.65	7.82	12.77
2012	43.47	20.26	8.92	9.84					
2013	42.28	33.17	29.21	34.29	**2013**	9.65	27.31	22.40	19.26
2014	35.47	29.47	29.11	29.40					
2015	40.86	19.73	18.99	12.59					
2016	41.60	14.10	11.75	11.42	**2016**	14.38	83.22	10.22	19.47
2017	37.35	20.19	15.05	12.27					
2018	34.49	15.33	11.17	7.60					

Table 4. pH estimation RMSE results for literature based algorithms. Reported LIPHR values correspond to algorithm use that negates the date-specific application incorporated into the most recent update (Carter et. al, 2017). Notably values are highlighted in orange.

BOG					**WCOA**			
Year	Algorithm				Year	Algorithm		
	Alin	**LIPHR**	**LIPHR (dates)**	**CANYON**		**Alin**	**LIPHR**	**CANYON**
2015	0.180	0.053	0.034	0.039	**2011**	0.045	0.030	0.046
2016	0.138	0.064	0.069	0.069	**2013**	0.049	0.053	0.067
2017	0.220	0.097	0.101	0.123	**2016**	0.045	0.037	0.039
2018	0.214	0.021	0.022	0.032				

There are three notable observations that explain the comparably worse performance of the literature-based algorithms when applied to the BOG data. The first is the incongruity between the algorithms' geographic extent and BOG monitoring. These cruises include five stations within the Bay. In comparison, LIAR, LIPHR, and CANYON algorithms were all trained on a global dataset and Alin et al., 2012 was developed for Southern California, with Monterey Bay at the northern limit of the training data boundary. Additionally Gray et al., 2011 is a simplistic linear model based off data found at just one mooring in Monterey Bay.

Secondly, there is a noticeable improvement in RMSE values for both TA and pH predictions in 2018 (Tables 3 & 4). The visual comparison between actual and predicted values of total alkalinity across years, further highlights this improvement (Figure 8). A possible explanation for this change is a difference in lab settings. Starting in early 2018, MBARI staff and facilities began running biogeochemical analyses (i.e. pH, DIC, TA, etc) on all BOG samples. Prior to this, the analytical work was done at UC Davis, Bodega Bay. Additionally, 2018 data showed a smaller range in actual TA values, which could be due to the shift to MBARI labs or yearly variation (Figure 8).

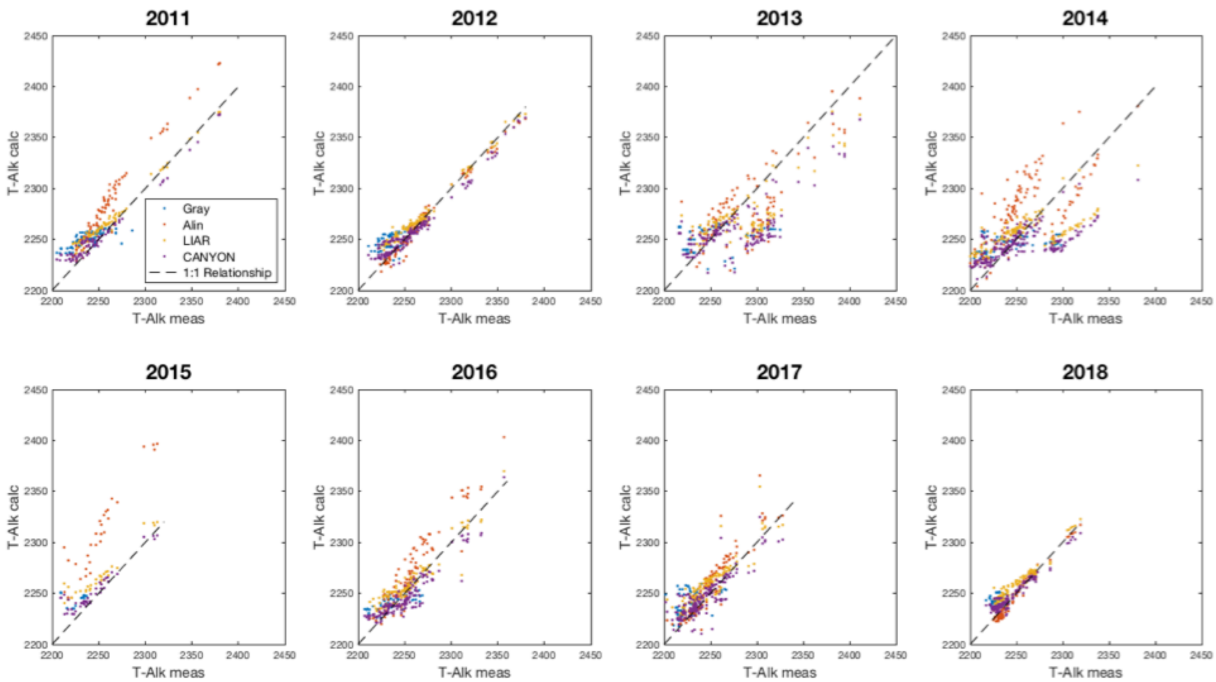


Figure 8. Performance of TA-predicting literature algorithms when applied to BOG dataset. Dotted black line indicates 1:1 relationship between predicted (calculated) and measured values.

2. <u>Monterey Bay-Specific Algorithm Development</u>
The third and final observation of BOG-applied algorithm performance coincided with the development of the Monterey Bay region-specific algorithms. Initial TA-focused MLR development resulted with lower r-squared values when compared to other parameters. Inspecting the relationship between predicted values and the validation dataset showed a distinct section of the data that fell below the 1:1 relationship cluster (Figure 9A). A likely explanation for this irregularity was the presence of multiple water sources within the BOG data. Physical characteristics (i.e. temperature, salinity, depth), collection location, and cruise couldn't distinguish multiple sources. Instead, the physical oceanography of Monterey Bay and a unique climatic event provided insight.

In the Monterey Bay, there are two major offshore, southward-flowing current systems – the California Current and the California Undercurrent (CUC). Normally, the two are best distinguished by depth; the undercurrent generally exists below 150m (Breaker & Broenkow, 1994). However, in the winter when persistent northwesterly winds that usually promote upwelling weaken an can cause “a reversal in the coastal ocean to northward flow at the surface”(Gangopadhyay et al., 2011), which some authors refer to as the Davidson current and others recognize as the surfacing of the CUC.

Starting in early 2013, California experienced an abnormally long drought due to a climatic event colloquially known as ‘The Blob’. This period was caused by a robust increase in the magnitude and persistence of a high-pressure system, nicknamed the Ridiculously Resilient Ridge (RRR), that formed along the western coast of the United States and weakened upwelling promoting winds (Swain et al., 2016). Normally a subseasonal occurrence in the winter months, the RRR intensified and lengthened the period of weak upwelling and caused the persistence of a large swath of warm water – The Blob (Swain et al., 2014; Swain et al., 2016).

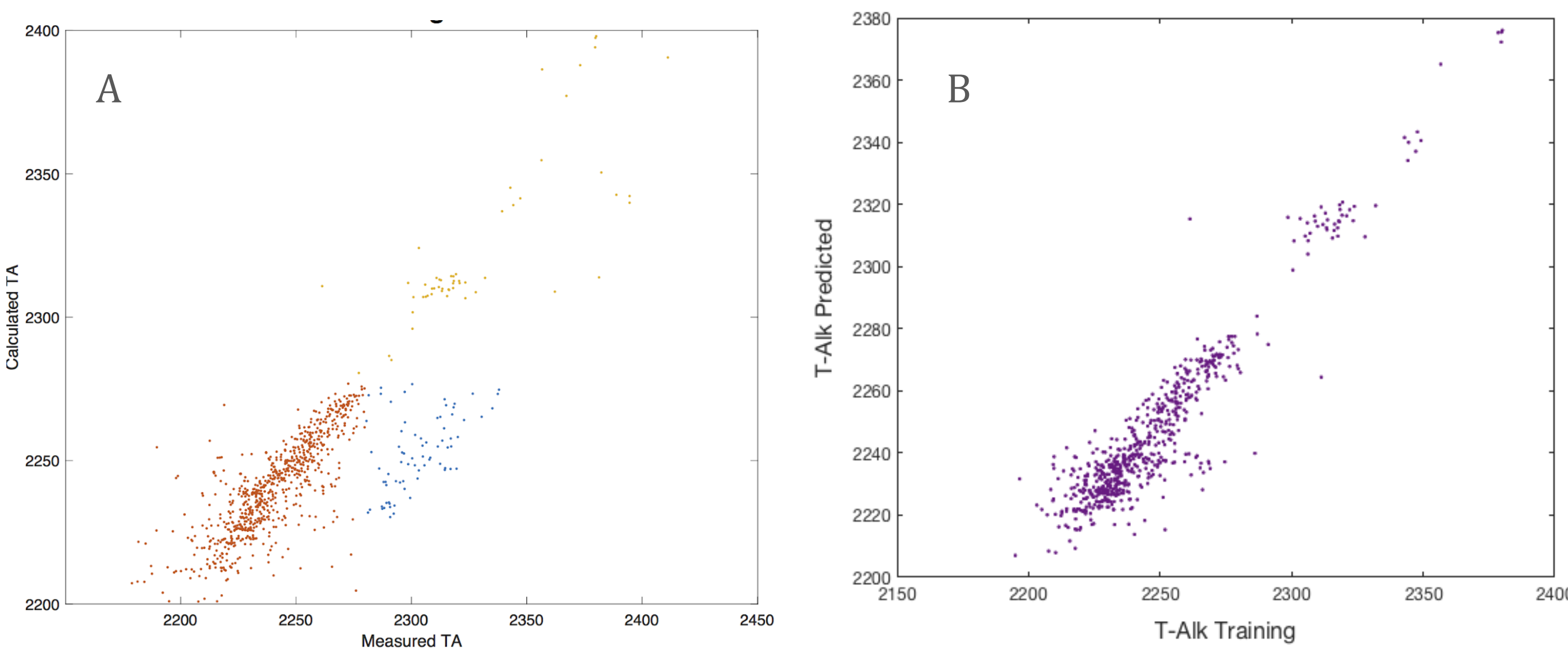


Figure 9. Performance of TA-predicting developed algorithm when applied to BOG dataset. (A) Includes all data years, 2011-2018. Colors distinguish sections of data. Red – low predicted TA values, low actual TA measurements; yellow – high predicted TA values, high actual TA measurements; blue – low predicted TA values, high predicted TA measurements. (B) Excludes data from 2013 and 2014 Blob years.

Given the relationship between CUC flow and upwelling dynamics, it's likely that the RRR s also caused CUC surfacing to persist longer than in normal years. Thus the BOG data from t period was able to depict a normally subtle and seasonal variation. As the CUC surfaces it b up deep water with likely higher TA concentrations. This, in addition to the presence of un warm waters along the coast offer reasons as to why multiple water sources – and differin values – showed up in the BOG TA dataset. Filtering the BOG data to exclude data from the period of 2013-2014 (based on precipitation data – Figure 10), confirms this theory. With Blob-exclusion the visual patterns of the data improved (Figure 9B), as well as the RMSE a squared values (Table 5). Returning to the literature TA-predicting algorithms, their perfo also noticeably worsened during the Blob-anomaly years of 2013 and 2014 (Table 3, Figur

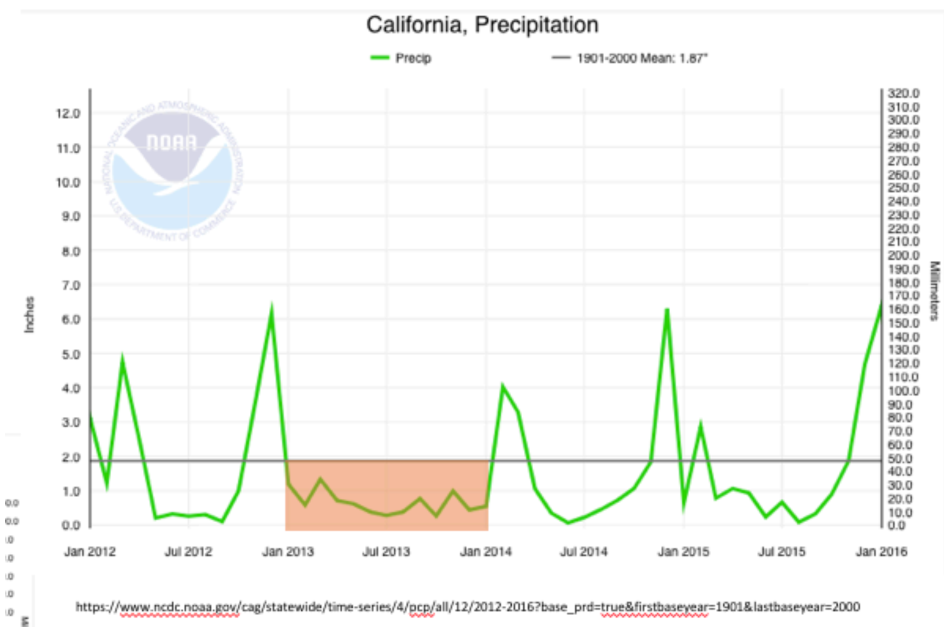


Figure 10. Monthly precipitation data from 2012 to 2016 for the state of California, in comparison to term mean. (NOAA). Orange rectangle indicates drought period.

Algorithm development for other carbonate parameters (NO_3, pH, and DIC) produced succ RMSE values and did not run into the same issues as total alkalinity (Table 5). Because the physical characteristics of the CUC are nearly identical to those of the California Current ar parameters like pH and DIC tend to vary more with temperature and salinity, the persister surfacing event likely did not have an impact. Resulting input variables and coefficients for parameters are presented in Table 5.

Table 5. Monterey Bay region-specific developed algorithms for multiple carbonate system parameters. All algorithms use a MLR approach that multiply various input variables by determined coefficients.

<table>
<tr><th></th><th>NO3</th><th>pH</th><th>DIC</th><th>TA</th></tr>
<tr><td>Input variables</td><td>x1 = salinity
x2 = temp
x3 = oxygen</td><td>x1 = salinity
x2 = temp
x3 = oxygen</td><td>x1 = salinity
x2 = temp
x3 = oxygen</td><td>x1 = salinity
x2 = temp
x3 = oxygen
x5 = pressure</td></tr>
<tr><td rowspan="5">Coefficients</td><td>-120.5522</td><td>7.2541</td><td>10.7688</td><td>282113.1513</td></tr>
<tr><td>5.0704</td><td>-0.0022</td><td>-0.1046</td><td>258.6002</td></tr>
<tr><td>-1.8327</td><td>0.0203</td><td>0.0193</td><td>-53.2659</td></tr>
<tr><td rowspan="2">-0.0746</td><td rowspan="2">0.0018</td><td rowspan="2">0.0015</td><td>0.0117</td></tr>
<tr><td>-280.7689</td></tr>
<tr><td>RMSE</td><td>1.9083</td><td>0.0513</td><td>19.9039</td><td>7.0073[A]</td></tr>
<tr><td>R2</td><td>0.9578</td><td>0.8959</td><td>0.9340</td><td>0.9127[B]</td></tr>
</table>

[A] Prior to data filtering value = 9.5404
[B] Prior to data filtering value = 0.6674

3. Algorithm Applications

Application of these algorithms to D. Rudnik 2017 glider data produced high-resolution contour plots of carbonate system behavior in the Monterey Bay. However, an exact validation of these algorithms' effectiveness was not possible at the time of this work. Though the trajectory of the glider data followed CalCOFI sampling line 66, this data was unavailable in the summer of 2018. Instead, the relative geographic proximity of NOAA WCOA data to Rudnik glider transect 1 (Figure 3), allowed for a reasonable qualitative assessment.

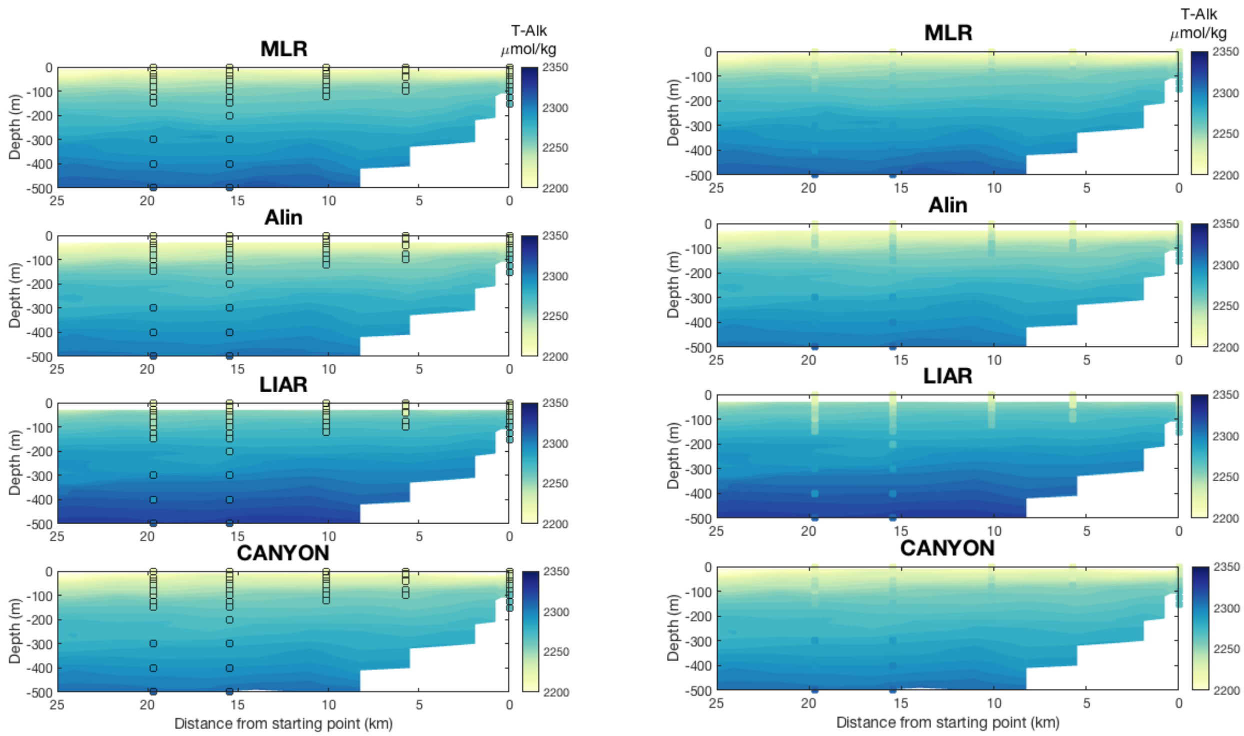


Figure 11. (A) Contour plot of total alkalinity for D. Rudnik glider transect 1 (3/28/17 - 4/13/17). Subplots show results of literature algorithms and developed MLR approach. Plotted circles correspond to discrete data from the 2016 NOAA WCOA cruise. (B) Shows the same data, but provides an easier visual comparison between glider and NOAA data. Per their application, Alin et al. 2012 and LIAR plots exclude surface waters.

Visual comparison of contour plots produced by the algorithms to NOAA WCOA data shows that the discrete data agreed best with the developed MLR and CANYON algorithms (Figure 11). These results are in alignment with the low RMSE values produced when the CANYON algorithm was applied to the BOG dataset. Additionally, the developed algorithm was trained on the BOG dataset, and therefore should be best suited for the Monterey Bay region when compared to the other literature algorithms. There is some agreement between the NOAA data and the applications of the other two literature algorithms. However, this agreement appears to only occur at depth, most likely due to complex variability of surface waters. According to their publications, the LIAR and Alin et al. algorithms are recommended for predicting measurements only below the ocean surface (Carter et. al., 2017; Alin et al., 2012).

Even though LIAR produced relatively low RMSE values when applied to the BOG dataset, the LIAR application showed the greatest disagreement in the contour plots (Table 2, Figure 11). In addition to surface complexity, nutrient levels also uniquely influence LIAR. Unlike the other four literature algorithms, LIAR includes nitrate and silicate as input variables – levels of which can vary based on upwelling conditions (Carter et al., 2017).

The resolution of the glider data was able to depict upwelling patterns – a contour plot of glider transect 2 explicitly illustrates the rise of deep, undersaturated ($\Omega_{Ar} < 1$) water rising to the surface (Figure 13). The timeline of glider data also coincides with the onset of upwelling on April

26, 2017 (Peterson et al., 2017; Figure 12). Since upwelling introduces nutrient-rich water up into the water column, this could explain LIAR's greater disagreement in shallower waters.

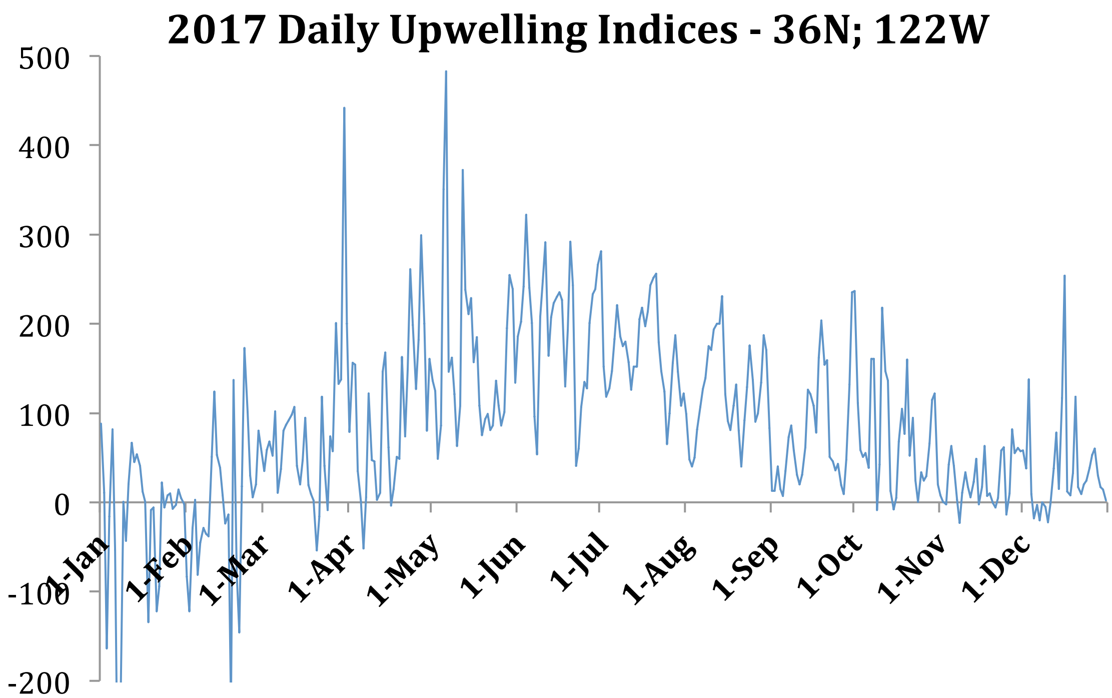


Figure 12. NOAA Pacific Fisheries Environmental Laboratory daily averages of upwelling indices. Data are derived from synoptic (6-hourly) sea level pressure gridded fields by PFEL for 15 positions along the west coast of North America. Position of these data is 36ºN and 122ºW – coordinates of Monterey Bay.

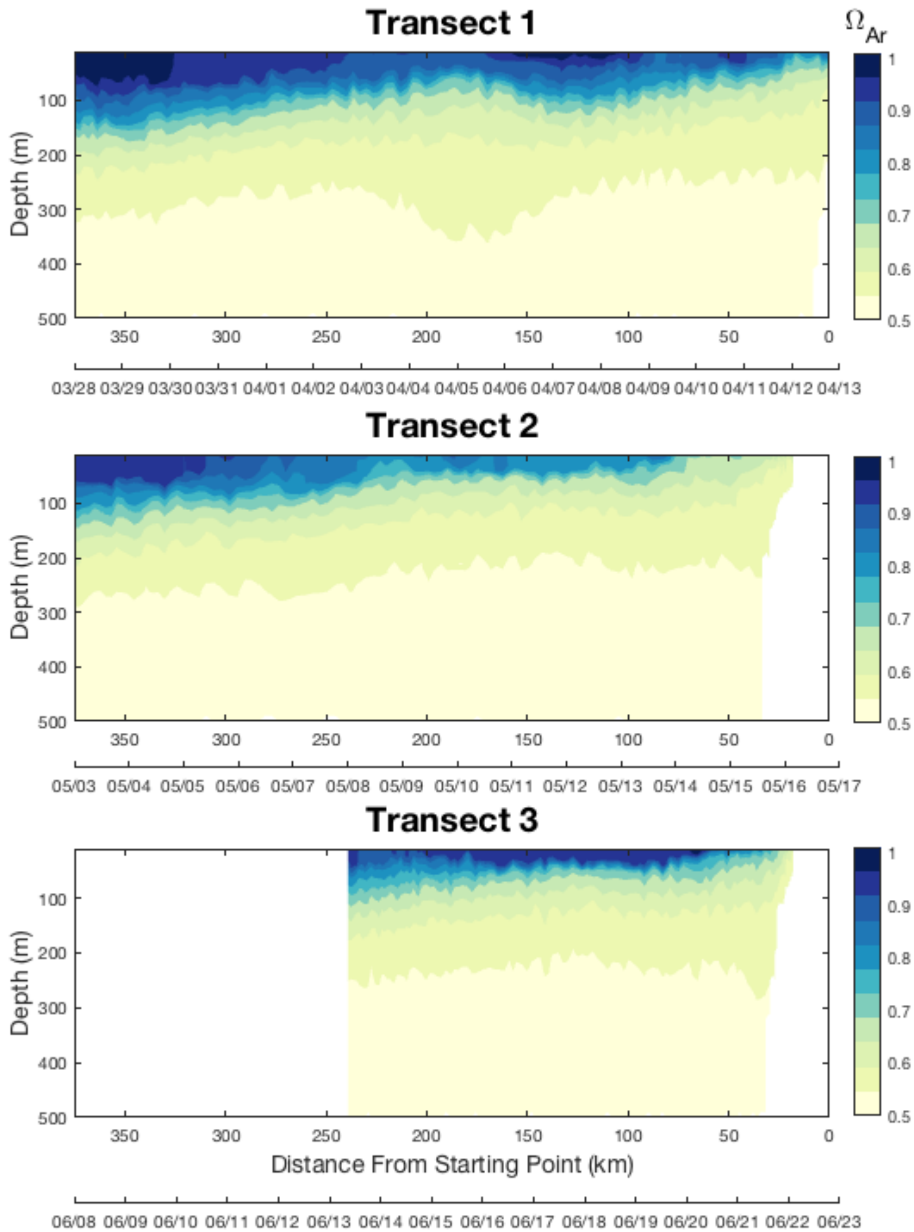


Figure 13. Contour plots of aragonite saturation state (Ω_{Ar}). Plots were developed after applying the developed MLR algorithm to D. Rudnik glider data. X-axis indicates both distance from shore and sampling time. Transect locations correspond to map shown in Figure 2B.

Applying algorithms to this glider data offers a unique opportunity to generate high-resolution depictions of the Monterey Bay carbonate system. Although, this application should be cautionary given the lack of a full quantitative validation. Another hesitation in applying these algorithms to the glider data, ties back to the organic alkalinity assessment of Monterey Bay. Because the influence of organic alkalinity could not be fully characterized, predicted TA outputs grom algorithms could be underestimates. Particularly at near shore areas, where Elkhorn Slough waters feed into the Bay and there are greater organic alkalinity sources (i.e. humic substances and suspended solids).

CONCLUSIONS & RECOMMENDATIONS

Organic Alkalinity

Because the WCOA NOAA organic alkalinity analysis was only able to report +5 umol/kg median organic alkalinity from 95% confidence interval and the location of significant stations were clustered on top of one another, the shown organic alkalinity is most likely not significant and instead some instrument/analyst error. Therefore, organic alkalinity is not a concern in these coastal ocean areas. However, looking at near shore estuarine environments did show more likelihood organic alkalinity presence.

A small subset of Monterey Bay data did not indicate any conclusive influence of organic alkalinity, though sampling from Elkhorn Slough did show significant results. To fully confirm the impact of organic alkalinity on the Bay system, actual nutrient levels of the discrete samples should be implemented into the analysis. Additionally, analyzing BOG data for a longer time frame than the 6 months between 2017 and 2018 would be highly recommended.

Algorithm Testing and Development

The pre-existing algorithms sourced from the literature, showed successful application to the NOAA WCOA dataset, which shows that they extrapolate well into the coastal areas along the West Coast of North America. However, these algorithms did not show convincing application to predicting TA and pH in the Monterey Bay region prior to 2018. From 2011-2017 resulting RMSE values were rather high. The subsequent improvement in 2018, when samples began being analyzed at MBARI facilities, indicates that future data points from the BOG dataset could be successfully incorporated into algorithm predictions.

Development of a Monterey Bay-specific MLR algorithm revealed that the BOG dataset captured a prolonged shift in coastal current dynamics during the 2012-2014 Blob phenomenon. The Blob dynamics likely extended surfacing of the California Undercurrent – a normally seasonal occurrence – and upshifted total alkalinity measurements in the BOG dataset. Filtering out these values produced successful RMSE values from the developed algorithm, though is a helpful reminder that algorithm predictions cannot account for all of the variability inherent in environmental processes.

Applying all algorithms to the pioneering 2017 glider data generated detailed depictions of the Monterey Bay carbonate system in the form of contour plots. These plots allowed for initial qualitative confirmation, showing that the developed and CANYON algorithms effectively predicts carbonate parameters in Monterey Bay.

Future Work

SFSU provided discrete samples from San Francisco Bay for similar organic alkalinity investigation, and initial analysis was also conducted in the summer of 2018. A similar ecosystem that is surrounded by metropolitan areas, the SF Bay is another environment where organic alkalinity could have a significant influence. Continued sampling and a full organic alkalinity assessment would provide an interesting context in characterizing the carbonate system of bay environments along the coast of Northern California.

The developed algorithm work did not entail a thorough quantitative validation when applied to the D. Rudnik glider data. At the time, CalCOFI line 66 data from 2017 was unavailable, though it is now readily available through the group's hydrographic database (1949-2017, http://calcofi.org/ccdata.html). Using this data to validate the application of both the developed and literature-based algorithms to the glider data would provide a constructive follow-through on this work, and motivate further applications. This would be especially useful in collaboration with the efforts of the chemical sensor group at MBARI as well as future glider deployments.

ACKNOWLEDGEMENTS

Special thanks to Andrea Fassbender for her mentorship and encouragement, and to George Matsumoto and Linda Kuhnz for organizing and facilitating the summer internship program. Additional thanks to Fassbender/Takeshita lab members: Yui Takeshita, Jacki Long, Joe Warren, Keaton Mertz, and Marguerite Blum. This research was made possible through their support and hard work along with the David and Lucile Packard Foundation, whose funding makes the work MBARI does possible. The other 2018 summer interns and Dana Lacono also deserve a special accommodation for their part in making the summer such an incredible experience.

REFERENCES

1. Alin, S. R. *et al.* (2012). Robust empirical relationships for estimating the carbonate system in the southern California Current System and application to CalCOFI hydrographic cruise data (2005–2011). *Journal of Geophysical Research: Oceans* 117.

2. Bradshaw, A. L. & Brewer, P. G. (1988). High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration. 2. Measurements on standard solutions. *Marine Chemistry*24, 155–162.

3. Breaker, Laurence & W. Broenkow, W. (1994). The circulation of Monterey Bay and related processes. Oceanography and marine biology: an annual review. Vol. 32. 32.

4. Cai, W.-J., Wang, Y. & Hodson, R. E. (1998). Acid-Base Properties of Dissolved Organic Matter in the Estuarine Waters of Georgia, USA. *Geochimica et Cosmochimica Acta* 62, 473–483.

5. Carter, B. R. *et al.* (2018). Updated methods for global locally interpolated estimation of alkalinity, pH, and nitrate. *Limnology and Oceanography: Methods* 16, 119–131.

6. Cullison Gray, S. E. *et al.* (2011). Applications of in situ pH measurements for inorganic carbon calculations. *Marine Chemistry* 125, 82–90.

7. Davis, C. V. *et al.* (2018). Reconstructing Aragonite Saturation State Based on an Empirical Relationship for Northern California. *Estuaries and Coasts* 41, 2056–2069.

8. Dickson, A.G., C.L. Sabine, and J.R. Christian, ed. (2007). *Guide to best practices for ocean CO_2 measurements*. PICES Special Publication 3, 191 pp

9. Fassbender, A. J. *et al.* (2017). Estimating Total Alkalinity in the Washington State Coastal Zone: Complexities and Surprising Utility for Ocean Acidificatin Research. *Estuaries and Coasts* 40, 404–418

10. Gangopadhyay, A. *et al.* (2011). The California Current System: A multiscale overview and the development of a feature-oriented regional modeling system (FORMS). *Dynamics of Atmospheres and Oceans* 52, 131–169.

11. Hernández-Ayon, J. M., Zirino, A., Dickson, A. G., Camiro-Vargas, T. & Valenzuela-Espinoza, E. (2007). Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters. *Limnology and Oceanography: Methods* 5, 225–232.

12. Hunt, C. W., Salisbury, J. E. & Vandemark, D. (2011). Contribution of non-carbonate anions to total alkalinity and overestimation of pCO_2 in New England and New Brunswick rivers. *Biogeosciences* 8, 3069–3076.

13. Johnson, K. S., Needoba, J. A., Riser, S. C. & Showers, W. J. (2007). Chemical Sensor Networks for the Aquatic Environment. *Chem. Rev.* 107, 623–640.

14. Kim, H.-C., Lee, K. & Choi, W. (2006). Contribution of phytoplankton and bacterial cells to the measured alkalinity of seawater. *Limnology and Oceanography* 51, 331–338.

15. Kuliński, K., Schneider, B., Hammer, K., Machulik, U. & Schulz-Bull, D. (2014). The influence of dissolved organic matter on the acid–base system of the Baltic Sea. *Journal of Marine Systems* 132, 106–115.

16. Lewis E Wallace DWR (1998) MATLAB program developed for CO_2 system calculations. *ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee*

17. McLaughlin, K., *et al.* (2015). Core principles of the California Current Acidification Network: Linking chemistry, physics, and ecological effects. Oceanography 28(2):160–169, http://dx.doi.org/10.5670/oceanog.2015.39.

18. Swain, D. L., Horton, D. E., Singh, D. & Diffenbaugh, N. S. (2016). Trends in atmospheric patterns conducive to seasonal precipitation and temperature extremes in California. *Science Advances* 2, e1501344.

19. Takeshita, Y. *et al.* (2015). Including high-frequency variability in coastal ocean acidification projections. *Biogeosciences* 12, 5853–5870.

20. van Heuven, S., D. Pierrot, J.W.B. Rae, E. Lewis, and D.W.R. Wallace. (2011). MATLAB program developed for CO_2 system calculations. ORNL/CDIAC-105b. *ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.* doi:10.3334 /CDIAC/otg.CO2SYS_MATLAB_v1.1.

21. Waldbusser, G. G. & Salisbury, J. E. (2014). Ocean Acidification in the Coastal Zone from an Organism's Perspective: Multiple System Parameters, Frequency Domains, and Habitats. *Annu. Rev. Mar. Sci.* 6, 221–247.

22. William T., P. *et al. Ocean Ecosystem Indicators of Salmon Marine Survival in the Northern California Current*. (Northwest Fisheries Science Center, NOAA, 2017).

23. Yang, B., Byrne, R. H. & Lindemuth, M. (2015). Contributions of organic alkalinity to total alkalinity in coastal waters: A spectrophotometric approach. *Marine Chemistry* 176, 199–207.

SUPPLEMENTAL FIGURES

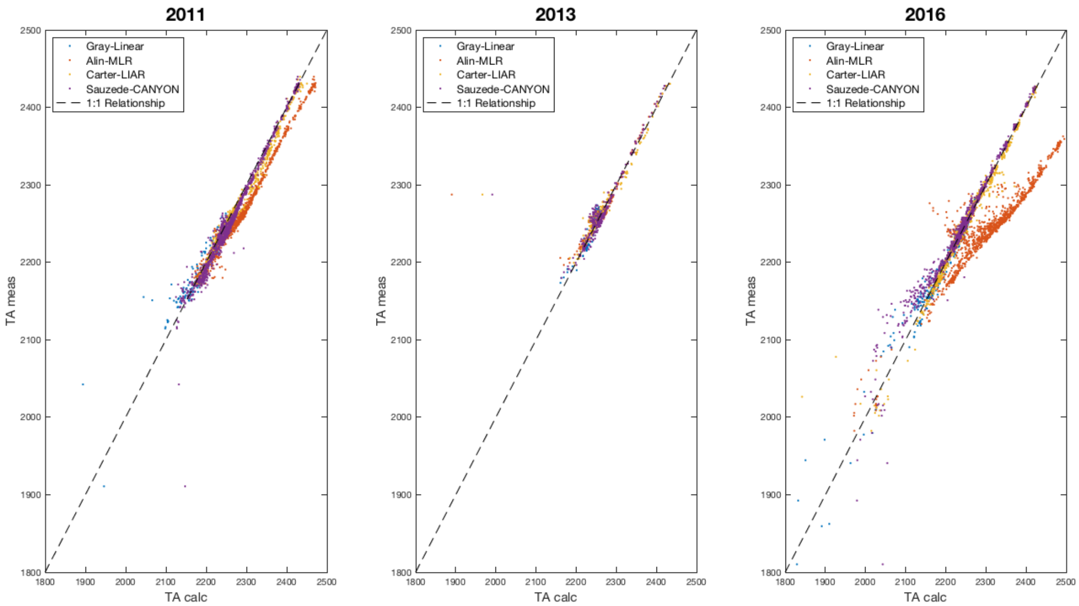


Figure S1. Performance of TA-predicting literature algorithms when applied to NOAA WCOA dataset. Dotted black line indicates 1:1 relationship between predicted (calculated) and measured values.

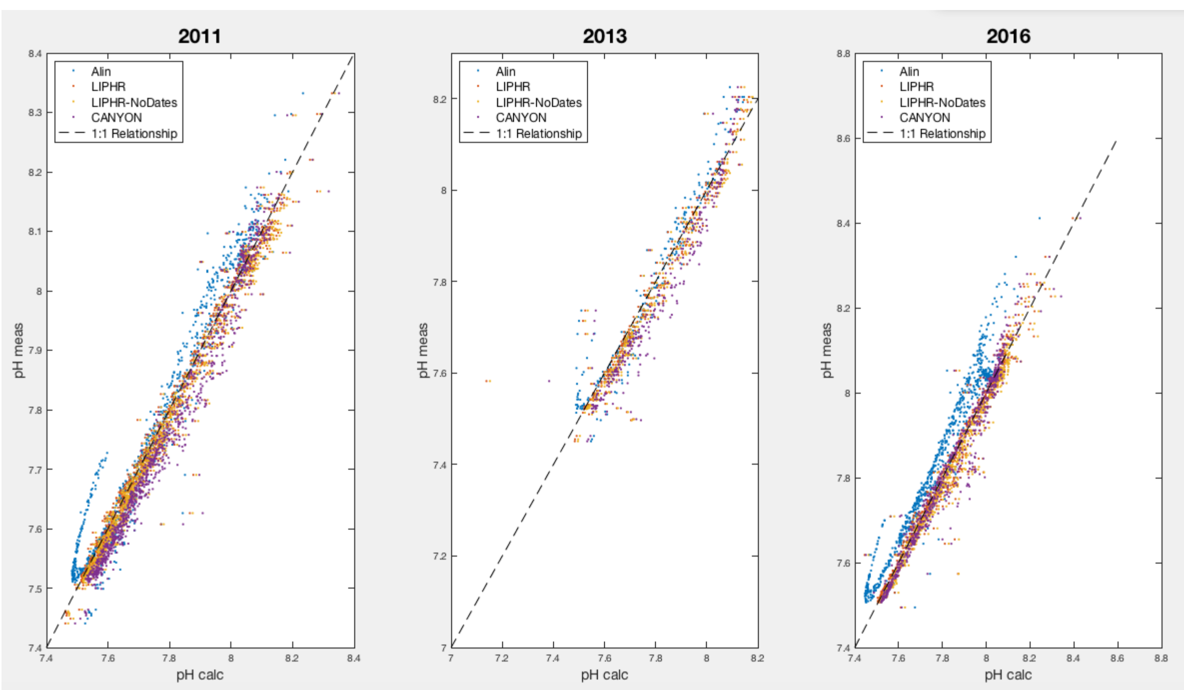


Figure S2. Performance of pH-predicting literature algorithms when applied to NOAA WCOA dataset. Dotted black line indicates 1:1 relationship between predicted (calculated) and measured values. LIPHR values are plotted twice to compare the difference when using the date-specific application and when not.