A Collaborative Assessment of Coastal Ocean Acidification Monitoring in Maine

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Standard Operating Procedures and Best Practices for the Collection of Continuous pH Data in Coastal Marine Environments

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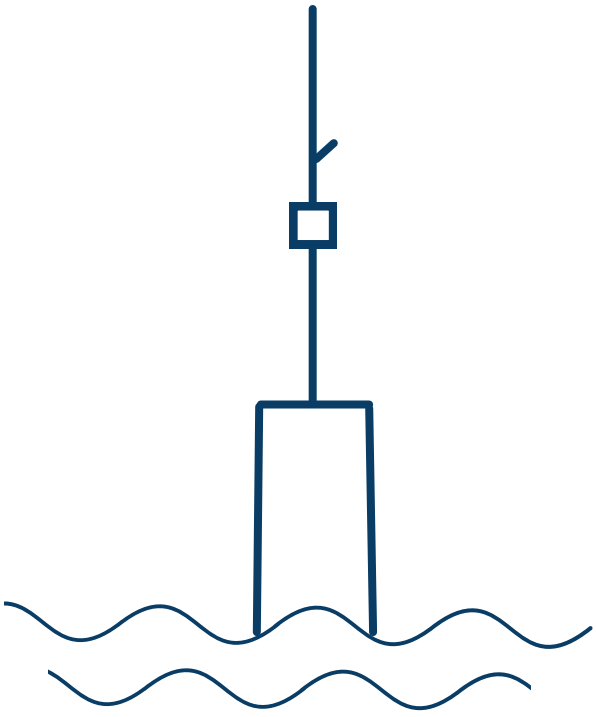

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Abstract

The ‘Sensor Squad’ of the Maine Ocean Climate Collaborative is the product of a 2023 Maine Coastal and Marine Climate Action Fund grant to conduct “A two-year pilot project designed to address and overcome technological barriers to ocean acidification data collection, develop protocols to elevate quality assurance and ensure comparable data, and meet regularly to discuss project results and data compilation”. The Squad consists of representatives from Friends of Casco Bay (FOCB), Wells National Estuarine Research Reserve (WNERR), and the University of New Hampshire (UNH). This report is a summary of their efforts to assess affordable, repeatable means of continuously monitoring ocean acidification.

Ocean and coastal acidification (OCA) are a growing concern, and efforts to monitor these changing and potentially damaging conditions are still emerging. This project will inform additional organizations that are working in collaborative ways to understand and track OCA and address goals of both the Maine Ocean Acidification Study Commission and the Maine Climate Council.

The project involves field and lab studies to evaluate a glass electrode pH sensor, and then investigations into the use of a regression model to calculate total alkalinity as a second carbonate parameter.

Introduction

During the past two centuries human activity has increased the concentration of carbon dioxide (CO_2) in our atmosphere through the burning of fossil fuels and changes in land use. Approximately 25 – 30% of atmospheric CO_2 is absorbed by the global oceans, and as the atmospheric concentration increases, the amount in our oceans rises as well. This increase in CO_2 alters ocean chemistry, shifting the concentration of hydrogen ions higher while decreasing the amount of important carbonate minerals, and resulting in ocean acidification (Feely et al., 2004). Closer to shore, freshwater inflows and biological productivity can exacerbate this issue, driving coastal acidification as these local influences also contribute to a shift in carbonate chemistry (Wallace et al., 2014).

The combined pressures of ocean and coastal acidification (OCA) can adversely impact many marine species, particularly those that live in coastal areas, and especially those that use calcium carbonate to build shells (Waldbusser et al., 2015). By 2050, models suggest that the northeast will be below the threshold for shell production for much of the year, especially near the bottom in coastal waters (MCC STS. 2020). It is therefore important to develop long-term continuous monitoring sites and platforms to improve our understanding of the timing and frequency of acidification in these nearshore and estuarine regions.

Coastal carbonate chemistry monitoring encompasses four key parameters: pH, the concentration of hydrogen ions and a measure of acidity; total alkalinity (TA), the buffering capacity of seawater; pCO_2, the partial pressure of carbon dioxide; and dissolved inorganic carbon (DIC), the total concentrations of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and carbon dioxide (Dickson et al, 2007). If any two of these four parameters are known, the other two can be estimated along with the saturation state of calcium carbonate or omega (Ω). However, some parameter pairings are better than others when making these estimates. Continuous *in situ* sensors for pH and pCO_2 are widely available, but unfortunately that parameter pair produces the highest uncertainty when used to determine the other parameters. Sensors for TA and DIC are not yet commercially available, leaving monitoring groups with few good options when choosing equipment to monitor OCA conditions.

Additionally, simply obtaining and using *in situ* pCO_2 and pH sensors to monitor OCA parameters can be difficult and prohibitively expensive for many coastal groups. Sensors which produce the highest-quality OCA measurements are much more expensive than more readily available sensors or data sondes. Ancillary measurements such as salinity, temperature, and dissolved oxygen are also needed to place OCA measurements into an ecological context, adding to the potential cost and complexity of a monitoring system. It is important to understand these challenges and limitations when coordinating or developing a monitoring program. One of the initial efforts of the Sensor Squad was to evaluate continuous monitoring of pH, which is the most commonly measured OCA parameter.

Tracking the relatively small changes in open ocean pH over long timescales (circa -0.02 pH decline per decade caused by the absorption of atmospheric CO_2) for climate-level monitoring is beyond the scope of this report. We chose to focus here on tools which can be used to monitor the larger OCA variability found in coastal and estuarine nearshore waters over tidal, diurnal, seasonal, and annual time scales. Variability of pH over these shorter time scales can be much larger (sometimes greater than 0.5) than the long-term, climate-driven ocean acidification trend.

The three technologies most readily available for pH sensors are ion-sensitive field-effect transistor sensors (ISFET, such as the Seabird Electronics SeaFET), spectrophotometric systems (such as the Sunburst Sensors SAMI-

pH sensor), and potentiometric glass electrodes (such as found on the YSI EXO2 sonde). Each approach has strengths and weaknesses.

The ISFET is very accurate but generally not cost effective for smaller monitoring programs. This type of instrument was used in some of our comparison work but was not considered a realistic option. Recent shortages of ISFET components have also highlighted the challenges of using this technology for routine monitoring. Not only is this technology relatively expensive for the target programs, but it requires an annual calibration and ISFET replacement that may result in large data gaps.

Spectrophotometric sensors are also very accurate, but the most affordable current option is a surface-only instrument (Sunburst Sensors iSAMI) and would not be applicable to the bottom-water programs at FOCB and WNERR. In addition, there were reliability and user interface concerns with these sensors when we started our work.

Glass electrode style pH sensors measure hydrogen ion activity rather than concentration like the ISFET or spectrophotometric methods. This type of pH sensor is the standard in coastal and estuarine monitoring. They are relatively affordable, user friendly and easy to deploy; however, glass electrode sensors have two significant issues. First, they do not hold a calibration for long periods of time, also referred to as “sensor drift”. Second, they use low ionic strength buffers for calibration, which are better suited to the freshwater environments they were originally designed for and less accurate in high ionic strength coastal and ocean environments. Use of these low ionic strength buffers results in glass electrodes measuring pH on the NBS scale, instead of the Total scale used by ISFET or Spectrophotometric sensors designed for marine pH measurements. Conversion between pH scales is not a simple process and adds some uncertainty to the converted pH values.

Given the goals and budgetary constraints of FOCB and WNERR, a review of these three pH sensor options found that despite their limitations the glass electrode was the most appropriate choice for our study, as long as any stability and precision issues could be addressed. Once this determination was made, our effort shifted to focusing on improving data quality and validating the glass electrode pH measurements.

FOCB and WNERR both boast long-term monitoring programs based on the use of a data sonde, a multi-parameter monitoring instrument that includes a glass electrode pH sensor. Both groups have over thirty years of experience with the data sonde, and both are dedicated to quality assurance. The benefit of using a data sonde is that water temperature, salinity, dissolved oxygen, chlorophyll, and turbidity can all be measured simultaneously along with pH in an affordable, user-friendly, and easily deployable package. With the decision to focus on the glass electrode for pH measurements, the Squad attempted to constrain the use of this existing instrument by trying to understand the inherent uncertainty and improve accuracy.

FOCB and WNERR worked to establish additional steps in their standard operating protocols that would result in best practices for increased pH sensor accuracy. These recommendations are outlined below, and include guidance in maintenance, calibration and deployment.

The work to examine sonde pH accuracy included collecting discrete bottle samples coincident with sonde deployment and several multi-week flow-through seawater tank comparisons against other instruments and bottle samples.

Map 1 - FOCB and Wells NERR monitoring locations along the western Maine coast. The UNH CML location is also shown.

FOCB collected bottle samples for pH analysis at three monitoring stations, and WNERR collected bottle samples at one station. Samples were collected every few weeks and analyzed spectrophotometrically at UNH using a benchtop spectrophotometer and meta-cresol purple indicator dye. This approach is the state-of-the-art for seawater pH measurements. The bottle sample results were compared to sonde pH data collected at the same time.

In April, June, and August of 2023 a series of pH sensor comparisons was conducted at the flow through seawater tank at the UNH Coastal Marine Lab. Bottle samples for pH analysis were collected as well as sensor pH data. During the August tank deployment calibration of the sonde pH sensors was checked against TRIS and AMP buffers, which are pH buffers prepared at the high ionic strength of seawater on the Total pH scale.

Alongside the sonde pH sensor validation efforts, the Squad also worked to identify a second OCA parameter to pair with pH. Since pH and TA make up the most accurate pairing of carbonate parameters when calculating additional parameters, and since TA sensors are not commercially available, we decided to investigate the use of a multi-linear regression model to estimate TA (Hunt et al., 2021). This model parameterizes the relationship between TA and several parameters that are currently measured by the data sonde (McGarry et al., 2021). Bottle samples for TA analysis at UNH were collected during FOCB and WNERR sonde deployments for this effort.

The resulting assessment of sonde glass electrode pH sensor performance, together with the capacity to estimate TA from other sonde measurements, could potentially allow "weather-level" OCA from a single instrument which is already widely used in nearshore monitoring. This should increase the capacity of smaller organizations to assist in regional efforts to track OCA trends in the nearshore environment as well as leverage decades of existing monitoring data.

Examining Sonde pH Sensor Accuracy

Laboratory-Field Sample Comparison

Our first effort compared sonde pH measurements to bottle pH measured spectrophotometrically in the lab at UNH. These lab pH measurements are highly precise (greater than 0.005 pH) and serve as a good baseline against which to evaluate sensor performance, thus for this study we consider the Lab pH measurements to be "correct" when compared to sensor pH measurements. After converting the lab pH values (made at a constant temperature on the Total pH scale) to values comparable to those measured by the sonde pH sensor (in-situ temperature, NBS pH scale), we calculated the pH Difference as:

$$pH\ Difference = pH_{Lab} - pH_{Sonde}$$

and we calculated the root mean square error (RMSE) as:

$$RMSE = \sqrt{\frac{\sum(pH_{Lab} - pH_{Sonde})^2}{n}}$$

where n is the number of samples.

The results from this comparison are shown in Figure 1. The calibration buffers used for pH sondes are typically certified to an uncertainty of ±0.01 pH units on the NBS scale. However, our observed pH uncertainty, measured by the differences between Lab and Sonde pH, was substantially higher. Our findings from this test are:

- The average pH Difference, or bias of sonde pH measurements when compared to lab measurements, was +0.07 for all YSI sondes, with one standard deviation equaling ±0.097. This indicates an appreciable offset between lab and sensor pH readings.

- The average pH Difference varied among sites, but not to a large degree. The variability of pH Differences was also not the same among sites, with one site showing more than twice the variance of the others (YSI Site D in Figure 1)

- The root mean square error (RMSE) between Lab and all Sensor pH measurements was ±0.11. The RMSE indicates the average magnitude of the difference between Lab and Sensor pH values, and thus gives an overall measure of sonde pH sensor uncertainty.

- There was no statistical relationship between date and pH Difference for any of the individual sites shown in Figure 1, or all sites grouped together, indicating that the pH Differences did not change consistently over time. This lack of change was shown by the slopes of linear regressions between date and pH Difference, which all returned p-values greater than 0.1.

- Further statistical analysis indicated that the sonde pH measurements were offset (i.e. biased) with respect to the lab pH measurements, by about -0.075 pH units (i.e. sonde pH was lower

than lab pH). When this offset is applied to YSI pH data, the RMSE of the resulting pH Differences was ±0.066.

- When using pH data from these sondes, we may report the pH as "**pH±0.11**" and incorporate an uncertainty of ±0.11 into any pH data analysis we perform, such as the calculation of other carbon system parameters, based on these monitoring station results. With lab assessment of YSI bias, we may report YSI pH as "**pH±0.07**"

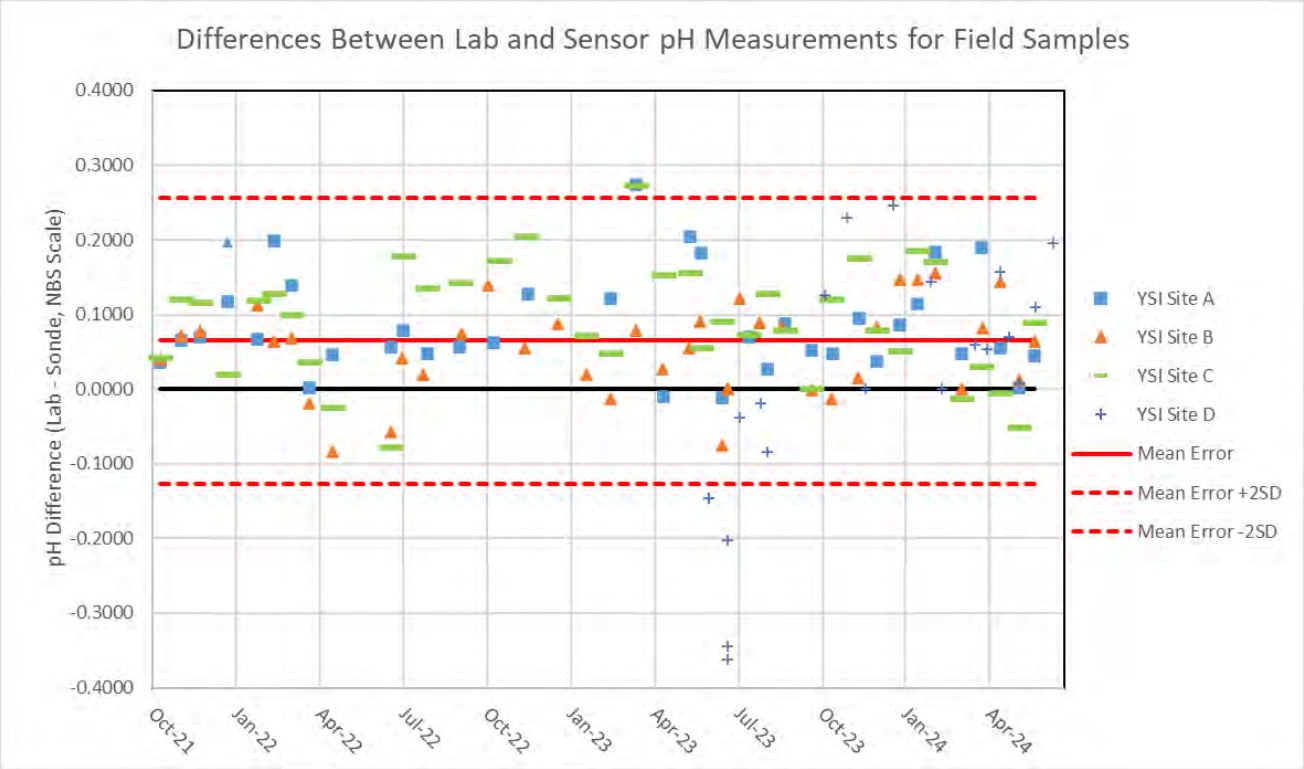


Figure 1- Differences between spectrophotometric Lab pH and Field sonde pH measurements at four sites for the project period. All differences are on the NBS pH scale at in-situ temperature and pressure. The aggregated Mean Error (i.e. bias) for all sites was +0.07 (solid red horizontal line), with one standard deviation of 0.097 (twice the standard deviation shows as dashed horizontal red lines). The Root Mean Square Error (RMSE) between all lab and sensor pH measurements, a measure of accuracy, was ±0.117.

UNH Coastal Marine Lab Tank Tests: Discrete Samples

While the monitoring station bottle samples provide one assessment of sonde pH sensor performance, some uncertainty is potentially introduced in collecting the bottle samples at the same time and depth at which the sonde is performing a pH reading. In 2023 the Sensor Squad performed three multi-week sonde pH sensor trials using a flowing seawater tank at the University of New Hampshire Coastal Marine Lab, in April-May, June-July, and August-September. YSI sondes from FOCB and WNERR, which were freshly calibrated on the NBS pH scale, were placed into the flowing seawater tank alongside a Seabird Electronics SeaFET sensor. During the three tests 11 discrete pH samples were collected for lab analysis, and pH Differences were calculated according to Equation 1. Note that for this report we deliberately do not associate particular YSI sonde pH data with FOCB or WNERR; we

consider variability between the YSI sondes as indicative of instrument performance under best practices, and not the skill or technique of individual operators. Our findings for this test were:

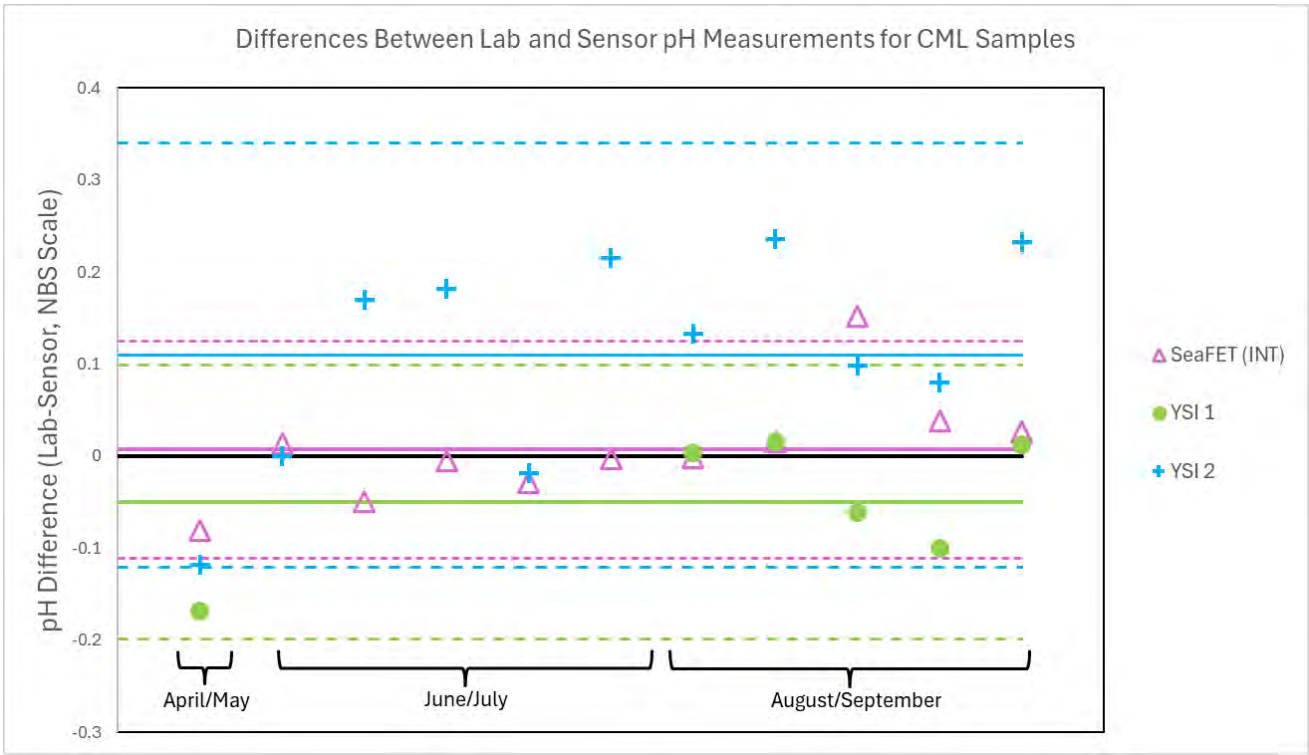


Figure 2- Differences between spectrophotometric lab pH measurements and sensor pH measurements during three tests at the UNH Coastal Marine Laboratory (CML). The mean offset for all samples was +0.007 for the SeaFET, -0.05 for YSI 1, and +0.11 for YSI 2. These mean values are shown as horizontal solid lines, while dashed horizontal lines show two standard deviations from the mean offset for each sensor. The root mean square error (RMSE) between lab and sensor pH was ±0.056 for the SeaFET, ±0.08 for the YSI 1, and ±0.15 for YSI 2. For the pooled measurements from both YSI sondes the RMSE between lab and sensor pH measurements was ±0.13.

- CML tank tests showed consistent differences among pH sensors (Figure 2). The SeaFET sensor agreed well with lab pH measurements, with a mean offset of 0.007±0.056 (the ±uncertainty represents one standard deviation of the pH Differences).
- YSI sensor 1 generally overestimated pH when compared to lab pH measurements, resulting in an average pH Difference of -0.05±0.08, while YSI sensor 2 generally underestimated pH when compared to lab measurements, resulting in an average pH Difference of 0.11±0.15. These results agree well with those we observed from Field Samples.
- Similarly, the RMSE between sensor and lab pH measurements was ±0.056 for the SeaFET, ±0.08 for YSI 1, and ±0.15 for YSI 2. Together, the combined results from the YSI probes gave a RMSE of **±0.13**, which supports the results from the Field samples presented in Section 1.1.
- It seems reasonable to expect an uncertainty (represented by the RMSE statistic) in YSI pH measurements of **±0.11-0.13** in general for coastal ocean sites when the probes are calibrated with standard NBS buffers according to recommended Standard Operating Procedures and the Best Practices described at the end of this report. Applying a correction based on bottle samples will reduce this uncertainty.

UNH Coastal Marine Lab Tank Tests: Sensor Comparison

Despite offsets between pH sensor readings and discrete lab samples, the sensors individually tracked the short and long term changes in pH well. This is highlighted in Figure 3, which shows results from the summertime CML test during June and July, 2023. Short-term cyclical changes in pH were driven by tidal mixing, while longer-term changes were driven by seasonal shifts in temperature, salinity, and the balance of biological productivity and respiration. Our findings from this sensor comparison are:

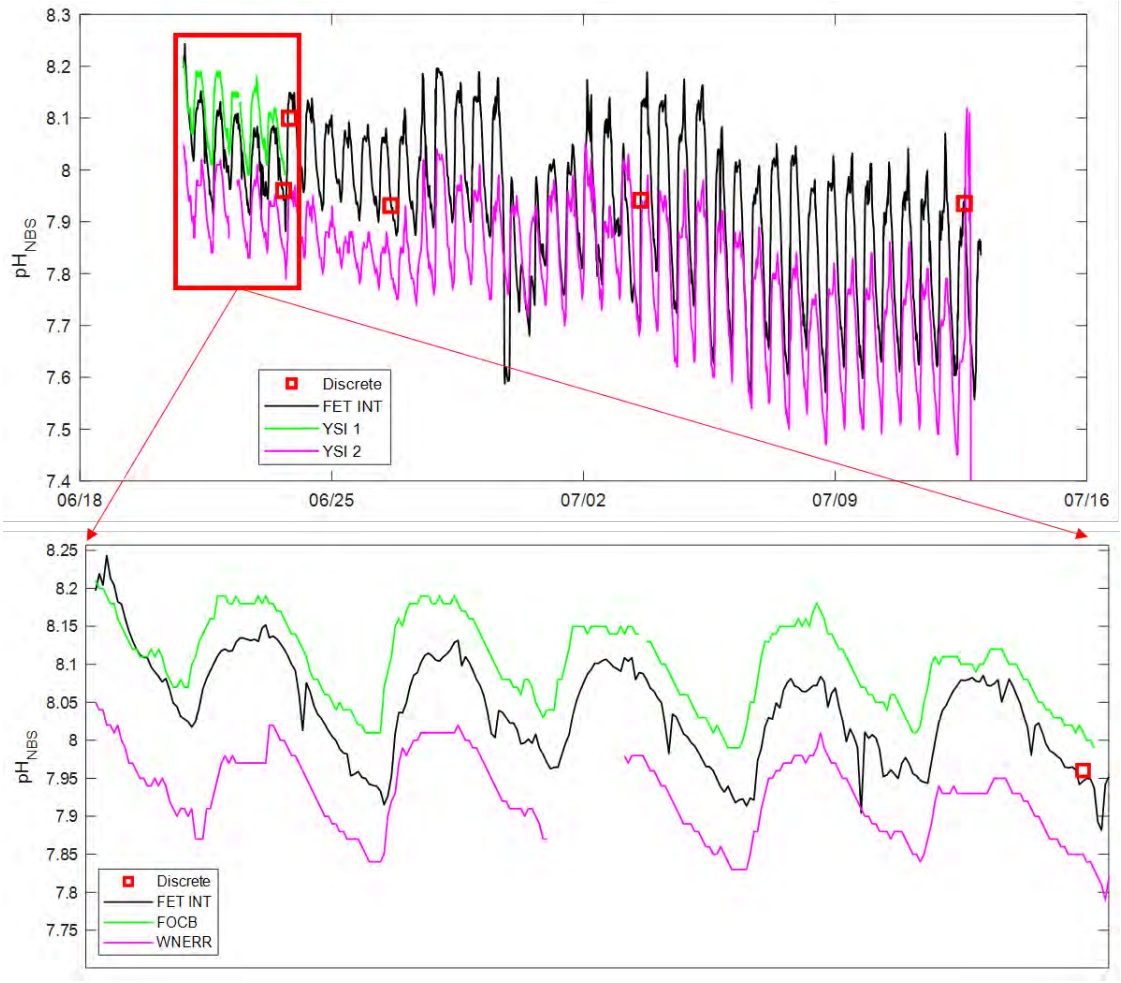


Figure 3- pH time series from the tank at the UNH Coastal Marine Lab in June and July, 2023. The YSI 1 (green line) failed shortly into the test, while the SeaFET (black line) and YSI 2 (magenta line) ran successfully. None of the sensor data in this plot are adjsuted to the discrete sample results. The top panel shows the complete timeseries, the bottom panel shows the subset of data marked by the red box in the top panel.

- It is clear that even carefully calibrated YSI sondes can disagree with discrete laboratory validation samples. We recommend collecting periodic lab samples during sensor deployments to help assess this disagreement.
- A simple offset subtraction can not only substantially improve the agreement between an individual sensor and the discrete lab measurements, but also between sensors as well. For example, we calculated average pH Differences between lab samples and sensor pH measurements for the three combined CML tank tests (Figure 2). When mean pH Differences

are applied to the sensor readings for the June-July test (Figure 4) the agreement among sensors improves markedly, and the YSI pH readings are mostly within the uncertainty bounds of the more accurate SeaFET sensor.

- Using discrete sample corrections which are specific to a particular deployment may increase sensor results further (i.e. applying a specific correction for samples collected during the June-July test, as opposed to the correction calculated for the pooled samples among all three tests).
- Even after correction, the response to changing pH conditions differed among sensors (Figures 4 and 5). While each tidal cycle produced similar changes in pH for every sensor, the SeaFET sensor often reached higher ‘peak’ pH levels when compared to the YSI sensor. This can especially be seen in Figure 5.
- Interestingly, the lower YSI pH readings for each tidal cycle seemed to agree much better with the SeaFET sensor, resulting in pH Differences closer to zero. This response difference could indicate a salinity-dependent effect on the YSI glass electrodes or some other interference we were not able to quantify. While most of the low-tide pH minima fell within the uncertainty bounds of the SeaFET sensor, indicating reasonable sensor agreement, the corresponding high-tide pH Differences were outside the uncertainty bounds and indicated worse agreement.

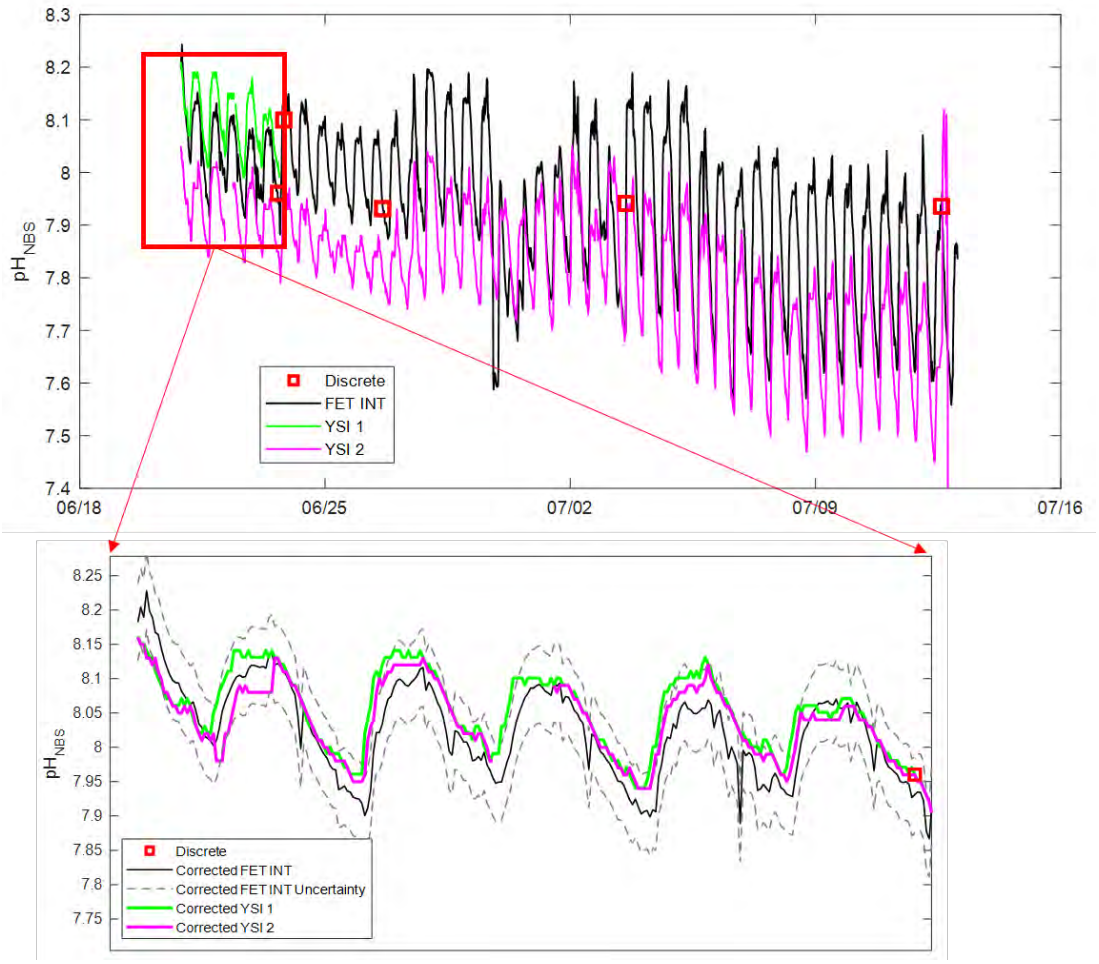


Figure 4- Corrected pH time series for the June-July 2023 CML tank experiment. The top panel shows the complete time series, while the bottom panel shows the subset of data outlined in the red box corrected using the discrete samples. The dashed lines in the bottom panel show the corrected "FET INT" pH readings plus or minus the RMSE uncertainty of all FET INT samples in the CML tank tests (±0.056, see Section 1.2.1)

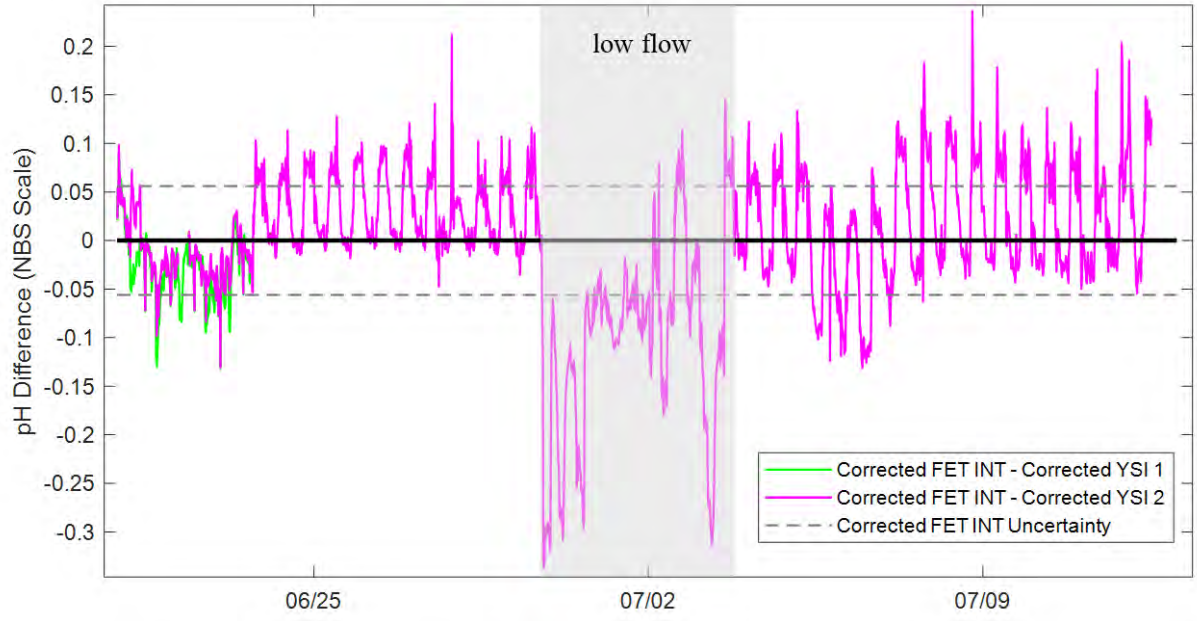


Figure 5- Differences between concurrent SeaFET and YSI pH measurements. YSI 1 failed early into the test (green line). The uncertainty bounds shown are those for the SeaFET sensor (i.e. ±0.056). The large negative differences from June 29-July 3 (grey box) may be attributed to low water flow to the SeaFET sensor during this time period, which affected the pH readings.

Application of synthetic seawater buffers to pH sensor calibration

A persistent challenge to using glass electrode pH sensors to monitor OCA conditions is the variable sensitivity of glass electrodes to ionic strength (reflected in varying salinity conditions). While the commercially-available buffers used to calibrate glass electrode pH sensors are prepared at low ionic strength as found in freshwater environments, OCA observations are taken at much higher ionic strength, presenting a source of considerable uncertainty. However, higher ionic strength pH buffers, calibrated on the Total pH scale (pH_T), are available from some research laboratories, or can be prepared by researchers in synthetic seawater (Dickson et al. SOP 6a, Dickson et al. 2007). Availability of these high ionic strength pH buffers presents a challenge to their routine use in wide-scale OCA monitoring. We obtained synthetic TRIS buffer (2-amino-2-hydroxymethyl-1,3-propanediol) from the lab of Dr. Andrew Dickson at the Scripps Institution of Oceanography, and AMP buffer (2-aminopyridine) from Dr. Robert Holmburg at the Downeast Institute. During the August-September tank test at CML we recorded YSI mV readings for both TRIS and AMP buffers and calculated pH_T data using either a single Tris or AMP value (assuming a theoretical Nernstian slope for the electrode), or the paired Tris and AMP values (which resulted in a non-Nernstian slope). Our findings from this test were:

- Calculating pH using only the AMP buffer gave the best results (average pHT Differences compared to the SeaFET of **+0.015** for YSI 1 and **+0.024** for YSI 2) and were well within the SeaFET sensor uncertainty (see Figure 6). When combined with the SeaFET uncertainty, the overall pH uncertainty resulting from calibrations with these seawater buffers was about **±0.064.**
- Average pH_T Differences using Tris buffer alone (-0.084 for YSI 1 and -0.075 for YSI 2) or both Tris and AMP buffers (-0.060 for YSI 1 and -0.074 for YSI 2) were similar, and were at the limits of or exceeding the SeaFET uncertainty
- The use of synthetic seawater buffers for YSI calibration offers measurement improvements similar to those achieved using discrete lab measurements to correct YSI pH data
- The availability of synthetic seawater buffers limits the wider adoption of this practice

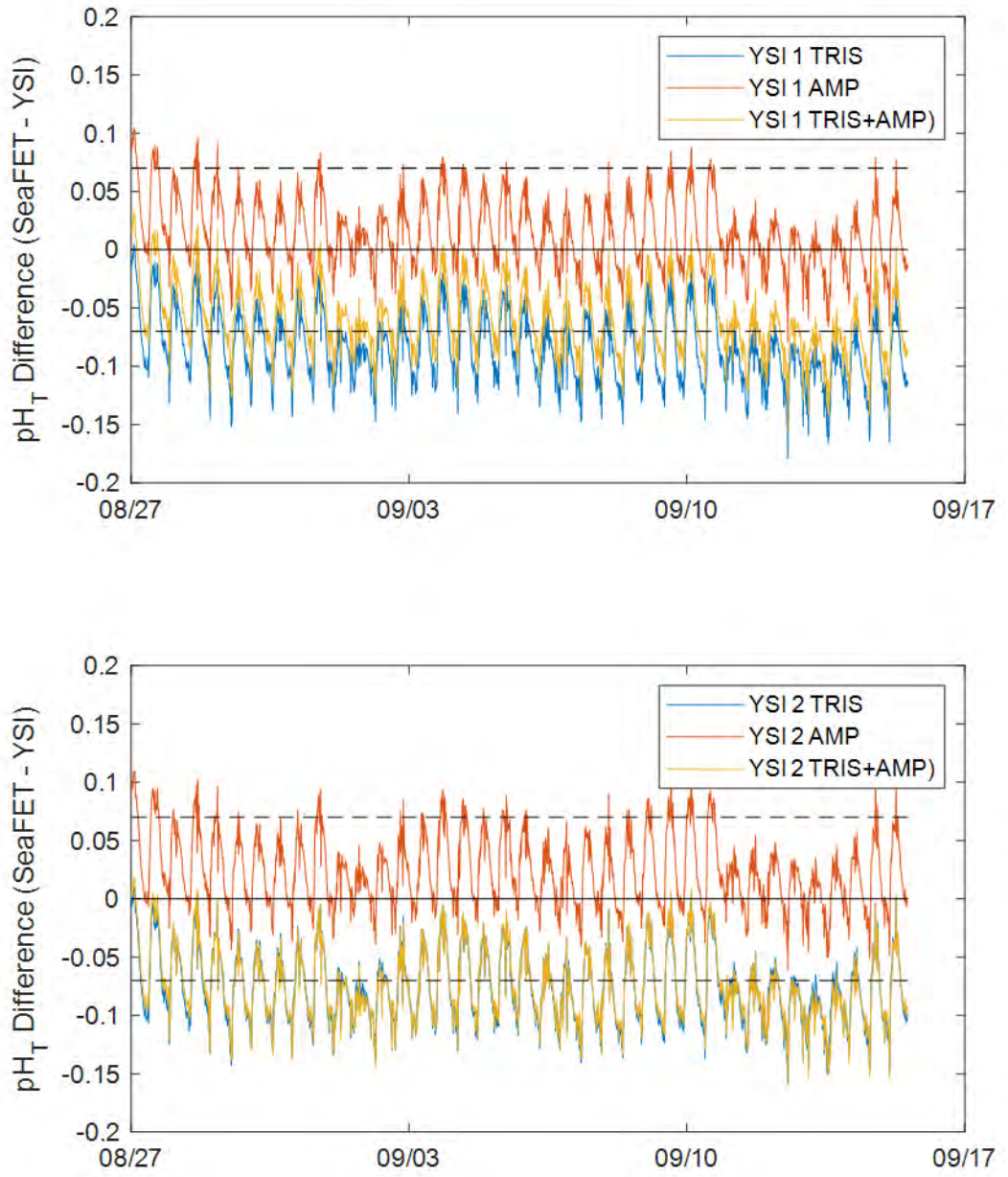


Figure 6- Differences between concurrent SeaFET and YSI pH sensor readings, when the YSI sensor is calibrated with high ionic strength buffers. Note that pH values are on the Total pH scale, as TRIS and AMP buffers are calibrated on the Total scale. Dashed lines indicate the observed SeaFET sensor uncertainty against discrete sample of ±0.07 pH units.

Using Sonde Measurements to Estimate Other OCA Parameters

As mentioned in the Introduction, pairing pH measurements with another OCA parameter allows the estimation of the entire inorganic carbon system. This means that one of three parameters can be paired with pH data for this estimation; however, the pairings are not all equivalent. Pairing pH and pCO_2 measurements, which are highly correlated with each other, yields unrealistically variable results. Dissolved Inorganic Carbon (DIC) and pH make a good pairing, but a relatively small number of labs have DIC analysis capabilities. Total Alkalinity (TA) is a more commonly measured parameter, and some studies have shown that Total Alkalinity (TA) can be reasonably modeled from commonly-measured parameters such as salinity, temperature, and oxygen (Hunt et al. 2021, McGarry et al. 2021). This opens the possibility of reasonably estimating TA from continuously-measured or forecasted coastal ocean variables. We collected lab TA samples and combined the resulting TA data with sonde data to produce simple multiple linear models of TA. Our findings for this exercise were:

- The most useful inputs to the TA models were salinity first, followed by some combination of water temperature, oxygen, and time of year
- Models developed by this project were better able to reproduce the TA than the regional model presented by McGarry et al. (2021), as shown in Figure 7 ("UConn model")
- The RMSE of modeled TA was **30-50 µmol kg^{-1}**, an uncertainty of about 1.5-3 %.
- This level of uncertainty may be reduced by re-developing models with more input data
- The abundance of salinity, temperature and oxygen data make modeled TA a compelling second carbonate system variable

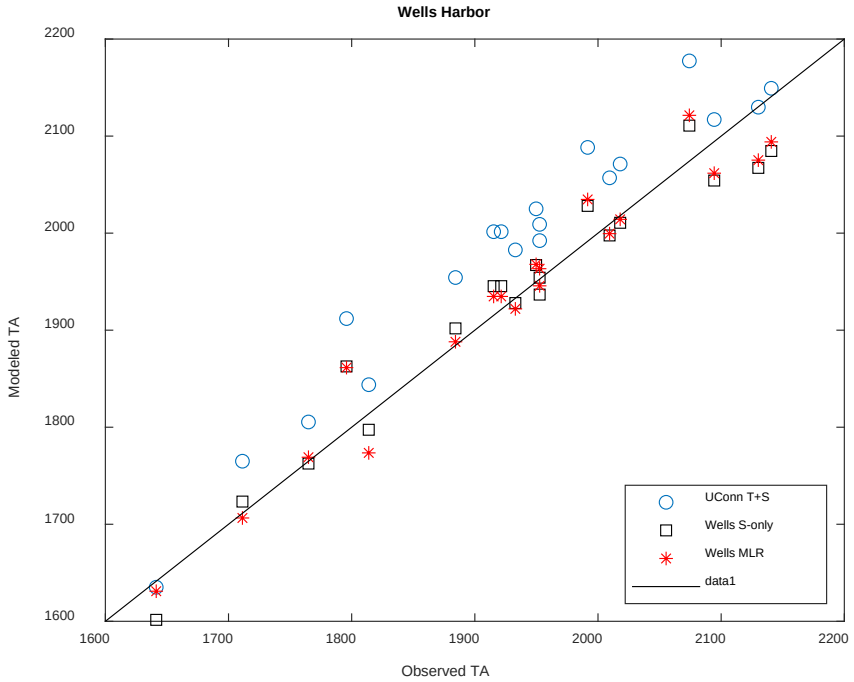


Figure 7-Total Alkalinity model for Wells NERR, with modeled TA from McGarry et al. 2021 ("UConn model"). All TA are in units of µmol kg^{-1}.

Implications of this Study for OCA Estimates

OCA studies do not just examine changes in pH, but rather look at changes in the carbonate system. One parameter that tends to be used as a sum indicator of OCA conditions is the saturation state of calcium carbonate (as aragonite), referred to as Omega-a or Ω_a. Omega-a is not measured directly, but rather is calculated from two other OCA parameters plus measurements of salinity and temperature. Each of these measurements carries a certain amount of uncertainty, which propagates through to the final estimate of Omega-a. We wanted to examine how our estimated uncertainties in measured pH and modeled TA might affect Omega-a estimates. Our findings are:

- pH measurement uncertainty represents the largest uncertainty in Omega-a estimates (Figure 8)
- The overall Omega-a uncertainty is substantially reduced if lab samples can be used to reduce the pH uncertainty
- The uncertainty of our modeled TA has a small impact on Omega-a estimates.

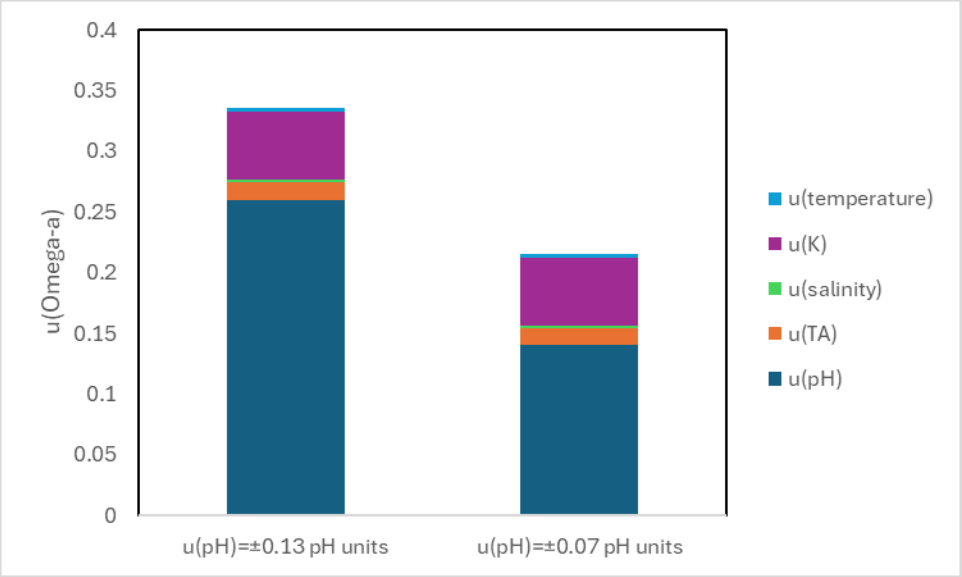


Figure 8- Sources of uncertainty in the calculation of aragonite saturation state (Omega-a), an important OCA parameter, at the Wells NERR site. The term u(K) represents the uncertainty of the carbonate dissociation constants.

Conclusions

The Sensor Squad set out to "address and overcome technological barriers to ocean acidification data collection and develop protocols to elevate quality assurance and ensure comparable data." From the start, we wanted to think about how a monitoring group with finite resources might develop an effective Coastal Ocean Acidification monitoring program, and what the data limitations of that program might be. Previous experience led us away from the use of pCO_2 sensors, and towards the use of readily-available pH sensors included as part of monitoring sondes such as the YSI EXO2.

The results collected as part of this project demonstrate that EXO2 sondes can reliably measure coastal ocean pH to an uncertainty of ±0.11 to ±0.13 pH units, when best practices such as those included in this report are followed [see table below]. Another pH sensor- the Seabird SeaFET- showed an uncertainty of ±0.056, or about half the pH uncertainty of the EXO2. The SeaFET can be an excellent choice for coastal pH monitoring, but its expense, requirements for ancillary components such as temperature and salinity sensors, and past challenges with service make it somewhat less accessible. Additionally, our work shows that the use of regular discrete validation samples with EXO2 pH sondes can improve uncertainty to a level quite close to that of the SeaFET. The use of synthetic seawater buffers to calibrate the YSI sondes also offered similar pH uncertainty improvements, but these buffers are difficult to obtain.

	YSI EXO2 (commercial buffers)	YSI EXO2 (corrected with discrete samples)	YSI EXO2 (seawater buffers)	Seabird SeaFET (factory calibration)
pH Scale	NBS	NBS	Total	Total
pH Uncertainty	±0.11 to ±0.13	±0.06	±0.064 (includes SeaFET uncertainty)	±0.056
Advantages	Relatively affordable	Simple correction procedure improves uncertainty	Improves uncertainty, reduces salinity errors	Accurate
Disadvantages	Increased uncertainty	Analytical lab help needed	Buffers not readily available	Relatively expensive, requires periodic component replacement

While pH monitoring is a valuable endeavor by itself in OCA monitoring, the ability to monitor or model a second OCA parameter unlocks a wealth of OCA information, including estimates of Ωa. Unfortunately, sensor technology is lacking in this area. pCO2 sensors have proved difficult (and the pairing of pH with pCO2 is problematic), and *in-situ* TA or DIC sensors are still not readily available for most applications. However, our results show that TA can be reasonably modeled from other YSI sonde parameters (specifically salinity, temperature, and/or oxygen, with time of year). This requires the collection and analysis of TA samples together with the development of a localized model (through a

relatively simple multiple linear regression approach). While not trivial, we believe this represents the most practicable approach available to a monitoring group to model a “second” OCA parameter to couple with pH observations. Some TA data for local model development may be already available in coastal databases such as the Coastal Ocean Data Analysis Product (CODAP, Jiang et al. 2021).

Together, lab-corrected pH data can be combined with modeled TA to estimate Ωa with a total uncertainty of about ±0.21. To put this result in context, we estimate that Ωa can vary at the Wells NERR site by up to 1.5 over the tidal cycle, and up to 2.1 over event-scale or seasonal time frames. This suggests we can use these approaches to examine Ωa changes with total estimated uncertainty approaching the “weather” criteria recommended by the Global Ocean Acidification Observing Network (Newton et al. 2015).

Standard Operating Procedures and Best Practices for the Collection of Continuous pH Data in Coastal Marine Environments

Recommendations and best practices for calibration, deployment, maintenance, and care of glass-bulb electrode style pH probes

Introduction

The following document is intended to provide guidance on the recommended methods or best practices for using "glass-bulb style electrodes" (pH probes), for the collection of continuous in-situ monitoring data in coastal marine environments. The goal of this document is to increase the accuracy and reliability of continuous pH data collected at long-term monitoring platforms, while using industry standard pH probes (YSI, In-situ, Eureka, Mantis, etc.). The steps and recommendations outlined in the document are a combination of the manufacturers recommended SOP's along with some "tips and tricks" garnered from the over 30 years of monitoring experience garnered by the authors of this document. **Users should always read and familiarize themselves with the manuals and SOPs provided by the manufacturer before proceeding.**

This document will cover both pre- and post-calibration procedures, deployments (both structural and procedural), probe diagnostics, care and maintenance, and other ways to improve the accuracy and reliability of continuous in-situ pH data.

Section One: Pre- and Post-Calibration in the Laboratory

In this section we will cover a variety of topics including the proper calibration techniques for glass electrode style pH probes. The information below is largely applicable to all make/models of commercially available pH Probes (YSI, Mantis, In-Situ, Eureka, etc.). The technology used in these probes is the same and they function very similar (if not identical) to each other. This section also includes some tips and suggestions for getting the best performance out of your pH probes. It is important to note that the "weakness" of these relatively cheap (cost) and commercially available pH probes is that not all pH probes come out of the box performing the same. It is important for the user to check each individual probe as well as their diagnostic parameters (covered later in this section), before calibrating and deploying in the field.

Considerations while performing your Calibrations

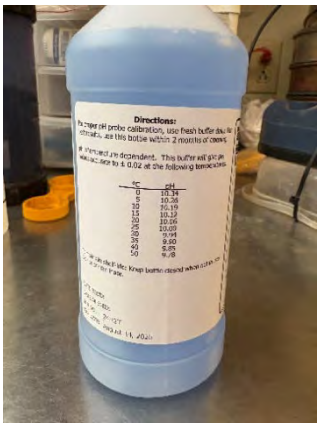
1) **Two Point Calibration**: Always calibrate your pH sensor with the two buffers, which "bracket" the range of pH you expect to see at your site. For more marine sites with little freshwater input, a 7/10 calibration is recommended. If your site is more brackish and

experiences freshwater intrusion/runoff, then a 7/4 calibration is recommended. You will always start any calibration with the 7 buffer.

2) **Dedicated calibration cup**: It is recommended that you keep a vessel or "container" (calibration cup) that is used only for pH calibration. This cup/container should be rinsed 3 times with De-ionized (DI) water between each pH buffer and then washed and dried well after each calibration.

3) **The "Three Rinse Rule"**: It is **possible to** introduce contamination or "dilution" to your pH buffers when switching from one buffer to the next. The probes themselves can retain quite a bit of liquid that can be transferred from one solution to **another**. To avoid this, the probes should be "rinsed" 3X with the buffer that they are about to be introduced to for calibration. Also, always remove any brushes or wipers from the system as they too hold a lot of liquid and can introduce contamination to your standards. The actual procedure for the "3 rinse process" is as follows:

    1. Pour a small amount of fresh pH 7 buffer into your calibration cup and rinse the probe(s) with pH7 buffer 3 times.
    2. Wipe down the probe(s) with a non-lint lab tissue (Kim-wipe)
    3. Fill your dedicated calibration cup with fresh 7 buffer and proceed with calibration
    4. Remove from 7 Buffer and rinse probe(s) 3X with fresh (deionized) water. Then pat dry as above.
    5. Repeat step #1 with either 4 or 10 buffer (this also rinses out your calibration cup at the same time!)
    6. Wipe down probes with lab tissue
    7. Fill your calibration cup with fresh 4/10 buffer and proceed with calibration



An important note regarding pH Buffers: ALWAYS use buffers that are made by the manufacturer. DO NOT re-use buffers or expired buffers. DO NOT try to make your own buffers unless you have considerable experience in doing so.

4) **Temperature Compensation:** pH is highly influenced by the temperature of the parent solution. Most pH buffers will provide a chart or table showing an "offset" or value for your buffer at a range of different temperatures. It is important to use this compensated value while calibrating and to try to have as consistent a temperature as possible where your solutions are being stored/used. Additionally, some calibration software provides an option to use automatic temperature compensation. If this option is available, it should be turned on.

5) **LET IT SOAK**: DO NOT rush your calibrations. Often you will get a message rather quickly that the values are stable and you are ready to proceed; this is usually not the case. By allowing your pH probe to "soak" in the buffer while it's calibrating for 10-15 minutes

greatly increases the accuracy of your calibration and allows your sensor to adjust to the solution. Do this for all pH values.

6) **pH Diagnostics**: A useful tool in assessing the overall performance of your pH probes is to record the "pH Milivolts" associated with each of your 2 buffers used in the calibration process. Each buffer will yield a number (in Milli-volts or Mv) after each step. **The "difference" in those two numbers should be somewhere between +/- 165-180 mV.** If not, the probe should be swapped out for a new one or "re-conditioned" according to the manufacturers SOP.

   Formula: pH mV= mV 10.00 – mV 7.00 = Delta slope

7) **Post Calibration Checks:** After returning from the field your probe should be checked for accuracy and any "drift" in the calibration during the deployment period (see further in this document for recommended deployment lengths). The probes should be cleaned of any visible debris/contamination, rinsed 3 times with pH 7 buffer, then placed in fresh 7 pH buffer and allowed to run "continuously" in this solution until the values stabilize. That value should be recorded along with the pH millivolts, and then the procedure repeated with the second buffer used (4 or 10).

Section Two: Deployment considerations

In this section we will cover some suggestions and best practices for field deployments of pH sensors for continuous collection of pH. This will include thoughts on deployment length, probe longevity, deployment structure, and site-based concerns/considerations. One of the key things to consider when collecting continuous monitoring data is to ensure that the data you are collecting is representative of the larger system you are trying to monitor, and that you are not creating a "micro-environment" where you are monitoring. This can happen for several reasons (fouling, reduced water flow, etc.), many of which will be outlined below.

1) **Site Selection/Concerns**: If selecting a new site to collect pH data, there are several things to consider when choosing a location within your system of interest (bay, river, estuary, etc.) These include but are not limited to:
   - Adequate flow and/or tidal flushing
   - Depth of deployment (is water mass stratified or well mixed?)
   - Is there existing infrastructure to deploy from?
   - Ease of access to site and permissions to access
   - Where in the system you deploy (spatial coverage, tidal range, etc.)
   - Understanding site "characteristics" including underlying geology, biological activity, anthropogenic inputs, etc.

2) **<u>Infrastructure</u>**: There are several factors to consider when thinking about what kind of infrastructure will be needed to deploy and maintain a long-term pH data collection platform. Here are a few things to consider:

Photo 1: Friends of Casco Bay deploys its sondes using a modified lobster trap.

- Stability and "longevity" of your station; Is the underlying substrate or infrastructure adequate to support your deployment for a long period of time?
- Ease of access; routine cleaning and station checks are critical to maintain a suitable "environment" for your sensors to perform in.
- Ensuring plenty of water flow in and around your sensors; This can be accomplished by drilling a series of 1" holes up and down your deployment tube (PVC) or deploying in a cage (photo 1) or other type of large mesh enclosure which will protect the instrumentation while allowing adequate water flow.

3) **<u>Length of Deployment:</u>** Keep them short (20-25 days)! How long a sensor is deployed can have major impacts on the quality of the data it collects, especially toward the end of a deployment. There are a number of factors that can influence your data quality if your sensors are left in-situ for long periods of time. The most impactful and common one is bio-fouling (growth of sessile organisms/algae on and around your probes) as well as probe (or calibration) drift.

- <u>Fouling of Sensors</u>: Biofouling is one of the biggest culprits when it comes to loss of data quality (photo 2). This is especially true in more temperate marine environments. Most instruments come with some kind of fouling prevention mechanisms, but they are not perfect and only help to stem the issue. The best way to ensure that your data is not affected by fouling is to <u>shorten your deployments to 20-25 days,</u> and to purchase and utilize anti-fouling technologies such as copper tape, anti-fouling sprays and paints, etc.

Photo 2: Tunicates and algae have collected on this data sonde. While the sonde's wiper has kept sensors relatively clean, the best way to reduce biofouling is to shorten deployment time

- <u>Fouling of station/infrastructure</u>: Even if your sensors are free of fouling, readings can still be affected by surrounding fouling communities usually associated with the infrastructure you are deploying from. Any PVC tubes or cages should be treated with anti-fouling paint and cleaned at least 2 times a year. The pilings or any other physical structure that you are using to secure your deployment should also be maintained and cleaned as well.

Using stainless steel brackets to move your deployment tube away from the pilings (photo 3) should be considered if possible.

4) Sensor Longevity (life): Although not all budgets will accommodate for this, we suggest that individual sensors are replaced at least once per year. pH sensors do not have a "shelf life". That is, the probe starts to "degrade" as soon as it is manufactured and packaged so do not buy probes in bulk to store in the lab.

Photo 3: Stainless steel brackets help keep this PVC deployment tube away from dock pier and wharf pilings. WENRR's sonde is secured at the bottom of this tube.

Conclusions

There are several factors that can affect the accuracy and reliability of your pH data collected in the field. Hopefully some of the suggestions and tips in this document will help ensure that the data you are collecting in the field is as accurate as possible. An old saying of "an ounce of prevention is worth a pound of cure" certainly applies here! Any steps an individual can take to help prevent drift during deployment or contamination in the calibration process, only helps to ensure the accuracy of the data in question. It is recommended that an institution engages in periodic grab sampling at their pH collection sites to run lab derived pH values to compare to the data from their glass bulb electrodes/pH instrumentation.

These best practices were compiled by the "Sensor Squad": (left to right) Jeremy Miller, Wells National Estuarine Research Reserve, Mike Doan, Friends of Casco Bay, and Christopher W. Hunt, Ocean Process Analysis Laboratory, University of New Hampshire.

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