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ABSTRACT OF THE DISSERTATION

**BEST PRACTICES FOR SEA-BIRD
SCIENTIFIC DEEP ISFET-BASED PH
SENSOR INTEGRATED INTO A SLOCUM
WEBB GLIDER**

by THEODORE PAUL THOMPSON

Dissertation Director:

Grace K. Saba

ABSTRACT

The processes driving coastal acidification are highly dynamic, especially in productive and economically valuable coastal marine ecosystems. Therefore, coastal acidification monitoring efforts require robust data collection and high-quality assurance and control. Observations of carbonate chemistry for detection of ocean and coastal acidification have traditionally been monitored through fixed moorings with sensors that measure pH and/or $p\text{CO}_2$ (the concentration of CO_2 in seawater) and ship surveys that utilize flow-through pH and $p\text{CO}_2$ sensors and collect discrete water samples to measure pH, total alkalinity, and dissolved inorganic carbon. However, the ongoing advancement of sensors integrated into underwater autonomous vehicles, such as gliders, provides the capability to detect fine spatial and temporal changes in the water column at a higher resolution. A recently developed glider sensor, the deep ISFET glider-based pH sensor, is currently demonstrating its ability to provide scalable ocean and coastal acidification monitoring networks with the capability of serving a wide range of users. This sensor was

developed through a coordinated effort between Rutgers University, the University of Delaware, Sea-Bird Scientific, and Teledyne Webb Research. Here, I present a best practices document for using a glider-integrated deep ISFET-based pH sensor on a Slocum Webb glider to collect high-quality pH data.

This thesis details aspects of sensor design and function as well as pre-deployment, deployment, and post-deployment procedures to be carried out during missions. The pre-deployment procedures include pH sensor calibration techniques recommendations for sensor conditioning prior to deployment, and glider mission setting options. For active deployments, I include recommendations for the collection of water samples for carbonate chemistry analysis as checks on the field precision and accuracy of the glider sensor as well as flight techniques for efficient glider sampling, energy usage, and biofouling minimization. The post-deployment procedures for delayed mode data processing include: calculating pH and salinity, evaluation of sensor response time lags, sensor time shift analysis (if applicable), QARTOD-based quality control, deriving total alkalinity from salinity-based total alkalinity relationships (if available), and extracting the full suite of carbonate chemistry parameters. This comprehensive best practices document can be used as an instructional guideline for a broad range of user groups.

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INTRODUCTION

Concentrations of atmospheric carbon dioxide, or CO₂, have increased nearly 45% since the Industrial Revolution (Dlugokencky, E. J., et al. 2021). The ocean absorbs nearly one third of the anthropogenic carbon in the atmosphere (Gruber et al., 2019), setting off a complex chain of chemical reactions that act to decrease ocean pH, or increase ocean acidity. This is termed ocean acidification, and it is occurring at a rapid rate as a result of the increasing amount of anthropogenic atmospheric CO₂ absorbed by the world's ocean. Since the Industrial Revolution, surface ocean pH has decreased by approximately 0.1 pH units and is projected to further decrease up to 0.29 pH units by 2100 under RCP8.5 (IPCC, 2020). Coastal regions can experience highly variable changes in carbonate chemistry, leading to the occurrence of acidification in localized areas at specific times (Goldsmith et al., 2019). Drivers of coastal acidification include inputs of freshwater with lower total alkalinity and higher concentrations of dissolved inorganic carbon, biologically respired or consumed CO₂, upwelling of corrosive bottom water, and mixing events associated with water masses lower in pH and total alkalinity (Goldsmith et al., 2019). Additionally, excess nutrient input into coastal waters promotes algal productivity that eventually sinks from the surface, leading to microbial degradation of organic matter that consumes large amounts of dissolved oxygen (hypoxia) and produces CO₂ (acidification) (Wallace et al., 2014). The reaction between atmospheric CO₂ and seawater produces carbonic acid. In water, carbonic acid dissociates into bicarbonate and carbonate ions releasing hydrogen ions. However, the ocean has a natural buffering process, whereby carbonate combines with hydrogen to form bicarbonate. Hence, increased ocean acidification results in a reduction of carbonate ions that calcifying organisms depend on to form their calcium carbonate shells and skeletons, made in one of the carbonate mineral phases of either calcite or aragonite (Gazeau et al., 2007). Ocean and coastal acidification can also impact other processes - metabolism, reproduction, development, acid-base regulation - in both calcifying and non-calcifying organisms (reviewed in (Saba et al., 2019)). Therefore, ongoing changes in seawater carbon chemistry led to a more acidified ocean that are projected to cause significant impacts on organisms and ecosystems.

Monitoring ocean carbonate chemistry is essential to better understand the drivers of acidification and the conditions that organisms are exposed too. However, the stochasticity of these coastal processes creates challenges in monitoring because it requires observations highly resolved in space and time. Ocean and coastal acidification have traditionally been monitored through fixed moorings with sensors that measure pH and/or *p*CO₂ (the concentration of CO₂ in seawater) and ship surveys that utilize flow-through pH and *p*CO₂ sensors and collect discrete water samples to measure pH, total alkalinity (TA), and dissolved inorganic carbon (DIC). These platforms tend to have either a

limited temporal resolution (research vessel) or a low spatial resolution (mooring) (Goldsmith et al., 2019). In addition, limited observation efforts include at least two of the four carbonate chemistry parameters needed to fully characterize ocean acidification (pH, DIC, TA, and $p\text{CO}_2$) (Pimenta & Gear 2018). Alternatively, Autonomous Underwater Vehicles (AUVs), specifically vertically-profiling gliders, can collect sustained high resolution carbonate chemistry data throughout the water column (Saba et al., 2019b; Wright-Fairbanks et al. 2020). Gliders are buoyancy-controlled low-powered vehicles that allow continuous data collection for weeks to months at a time. They can sample in depths ranging from 4 meters to 1000 meters and can maneuver through dangerous weather and the most challenging environments (Schofield et al., 2007). Gliders are scientifically adaptable, designed with designated bays to mount a variety of sensors for collecting data. Therefore, gliders can be equipped to map other parameters simultaneously to assess the relationships between carbonate chemistry, biological processes (e.g., phytoplankton biomass), and other potential environmental stressors (e.g., temperature, dissolved oxygen).

The recent advancement of pH measurement technology, specifically the collection of high-quality pH-data on depth-profiling floats [12, 13, 14], led to the development of the deep ISFET (Ion Sensitive Field Effect Transistor)-based glider pH sensor (Saba et al., 2019b). Through a partnership between Rutgers University, Sea-Bird Scientific, University of Delaware, and Teledyne Webb Research, a deep ISFET-based pH sensor was modified by Sea-Bird Scientific and integrated into a Slocum Webb G2 glider (Saba et al., 2019b). This pH sensor, coupled to a CTD unit, was reconfigured by Sea-Bird to fit into the existing CTD glider port utilizing the shared pumped system (Saba et al., 2019b). Measurements of salinity, pressure, and temperature, and knowledge of local or regional conservative salinity-TA relationships, can be used to estimate TA simultaneously with pH. Using these parameters as inputs in programs like CO2SYS (Heuven et al., 2011), other parameters of the carbonate system can be calculated, including $p\text{CO}_2$ and aragonite saturation state, Ω_{Arag} [9, 10]. Here we present an outline of the best practices and guidelines for operating an integrated deep ISFET-based pH sensor in a Slocum glider. The aim of these recommendations is to aid the scientific community and ensure high data quality from the pH sensor.

SENSOR DESCRIPTION

Sea-Bird Scientific significantly modified the design of its ISFET based pH sensor technology for operational glider applications. The pH sensor has a depth rating of 2000 meters, similar to biogeochemical Argo profiling floats. The pH sensor was reconfigured to fit into the existing rectangular glider CTD port sharing the pumped seawater

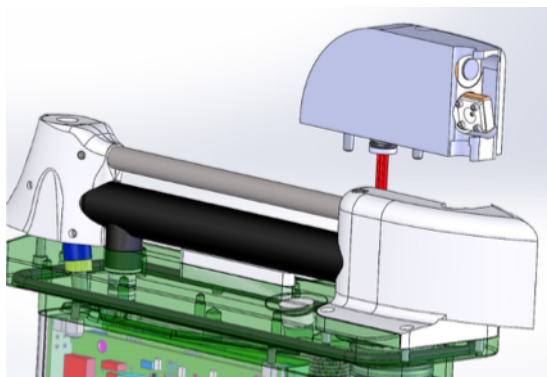


Figure 1. Deep ISFET-based pH sensor integrated with pumped CTD. Dark casing over “flowthrough” tubing.

system. The coupled integration creates a flow loop with seawater running over both the CTD and pH sensor elements. The ISFET, illustrated on the top right of Figure 1, is sensitive to light, therefore it is enveloped in a dark casing to block light.

A. Antifouling

Sensors submerged and operating in seawater for a period of time are susceptible to biofouling, the formation of complex layers of organisms on its surfaces (Delgado et al., 2021). The pH sensor described here uses three different approaches to minimize biofouling:

1. The use of dark casing around the seawater pump, CTD, and pH elements.
2. The addition of two antifoulant cartridges next to the CTD outlet. This antifoulant is approved by the United States Environmental Protection Agency for protecting the CTD cells in seawater.
3. Regular cleaning and re-calibration by the manufacturer. A sensor pH field accuracy (difference between discrete seawater using established seawater pH spectrophotometric methods [17, 18] and glider-based pH) outside of the ± 0.05 manufacturer specifications could indicate biofouling and should be addressed.

B. Power Draw

The pH sensor draws 36 mA at 15.75 Volts or 0.5 Watts. This is approximately 10-15% of the power budget of a typical 11.79 V lithium battery. The Slocum Glider Payload CTD consumes 240 mW continuously at 0.5 Hz taking a sample every two seconds. The pH sensor samples continuously 1 Hz, taking a sample every second.

C. Software

Sea-Bird provides a range of software to configure its hardware and sensors and process the data. SeatermAF© is the software used to run the CTD/pH unit. Sea-Bird Electronics (SBE) Data Processing is used to process the files from SeatermAF© and extract the data. Universal Coastal Interface (UCI) is the program that communicates with the pH sensor. The most recent version of these programs are available for download at the Sea-Bird Scientific software download site (www.seabird.com/software). The pH and other carbonate system parameters are loaded from the glider and calculated using MATLAB. This process is detailed in Section IX. Delayed Mode Processing.

SENSOR CALIBRATION

Sea-Bird Scientific performs a series of conditioning and calibration procedures on the deep ISFET-based pH sensor prior to shipping a new sensor. To calculate pH using a deep ISFET-based pH sensor, the individual sensor-specific pressure response function $f(P)$, temperature response constants k_2 , and conditioning offset k_0 must be derived in a controlled laboratory setting. Calibrations for $f(P)$ and k_2 are performed in a pressure vessel with a working fluid of 0.01N Hydrochloric acid (HCl). pH sensors undergo oceanographic temperature ranges (5-35°C) and pressure ranges (0-3000 psi) for 1 week.

During the k_0 calibration, the pH sensor is conditioned to natural seawater so that the molar ratio of Br/Cl of the electrode is in equilibrium with that of seawater. This process is achieved by flowing seawater over the sensor to allow the exchanging of chloride (Cl^-) ions in the silver/silver(I) chloride ($Ag/AgCl$) electrode with bromide (Br^-) ions. The change in pH is monitored with a spectrophotometer. Over time (3-5 days) the response of the pH sensor stabilizes (Figure 2), indicating that pH sensor has conditioned to the surrounding seawater. After the seawater is conditioned, the k_0 is calculated.

We recommend pH sensors be sent back to the manufacturer for cleaning and re-calibration at least once per year, and more often if deploying in productive coastal regions. Upon receipt of the returned sensor, Sea-Bird first conducts a cleaning procedure to remove debris caused by fouling and then re-calibrates the ISFET pH and CTD sensor units.

During this pH re-calibration, only the k_0 coefficient is revised. Note that the $f(P)$ and k_2 are not affected by repeated use.

PRE-DEPLOYMENT SENSOR CONDITIONING

New or “off the shelf” pH sensors need to condition or equilibrate to seawater collected at the planned glider mission location. When a pH sensor is introduced to local seawater conditions at the deployment site, the external electrode needs to equilibrate, or condition, to the new ionic concentration. This

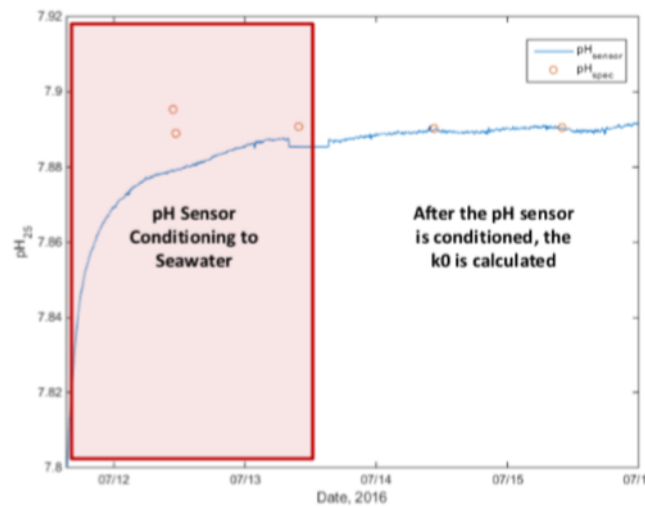


Figure 2. $k(0)$ is calculated by flowing seawater over the probe and measuring seawater pH with a spectrophotometer.

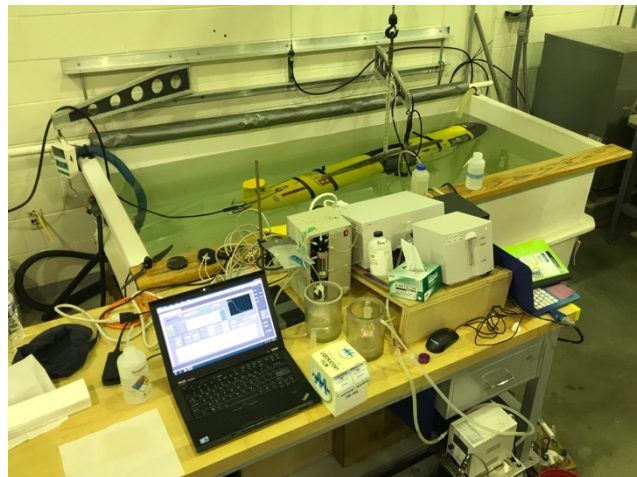




Figure 3. Photos demonstrating ‘in tank’ (top) and ‘flowthrough’ (bottom) conditioning. Photo credit: David Aragon.

process can take minutes to days (Saba et al., 2019b). In addition, polarization of the ISFET and counter electrode takes minutes to hours, and if connection between them is broken (e.g., loss of power, prolonged period of sensor being dry), the sensor will need to re-polarize (Saba et al., 2019b). conducted a series of tests to determine the glider-based ISFET sensor conditioning time after various time frames of dry exposure (i.e., out of seawater). Data from the glider submerged in a tank filled with locally collected seawater were transmitted in real-time via Freewave mode linked to Teledyne Webb Slocum Fleet Mission Control Software, and discrete seawater samples were collected periodically next to the glider and measured immediately on a spectrophotometric pH system. The pH sensor was considered conditioned after the pH measurements stabilized with minimum drift (± 0.0001 pH units hour^{-1} or ± 0.003 pH units day^{-1}). In trials where the sensor was dry for up to 24 hours, sensor re-conditioning once returned to seawater took less than 24 hours. But in trials where the sensor was kept dry for 3 days, sensor re-conditioning occurred after 3 days. Therefore, Saba et al. 2019b recommended a minimum of 5 days of soak time in natural seawater collected from the field location prior to a deployment if the sensor has been dry for more than 3 days.

There are two approaches to sensor conditioning. The first approach is soaking the glider with integrated pH/CTD sensor in a seawater tank. Alternatively, flushing the pH/CTD coupling with the pH sensor with local seawater is a useful approach without the necessity of soaking the entire glider in the seawater tank (Figure 3). This ‘flowthrough’ approach allows users to condition the sensor right up until placing the glider in the vehicle for deployment.

DEPLOYMENT

The following section describes the recommended guidelines for deploying the pH glider and collecting the discrete water samples for pH analysis (and optionally, TA and DIC) used to determine field accuracy of the glider pH sensor.

A. Glider and Sensor Tests

Once the glider is released at the deployment site, initial tests ensure the glider is receiving action codes and completing full dives. These tests also provide a GPS fix regularly when it surfaces so users can collect water samples for pH ground truthing in the proximity to the glider. A full description of pre-mission test codes, device commands and sensor commands are available in the Slocum G2 Glider Operators Manual pages 45-78 (Teledyne Technologies, 2019).

B. CTD and Discrete Water Sampling

At the deployment (and recovery) site, a CTD cast is conducted near the glider to select depths of interest for collection of seawater. At a minimum, a surface and near bottom sample are recommended (in duplicate), but additional sample depths are encouraged if there are features of interest (e.g., thermocline or intrusion of a distinct water mass). Discrete water samples are typically collected within 100 meters of the glider for comparison. Water collection can be conducted using equipment such as a Niskin bottle or a rosette fitted with multiple Niskin bottles and a CTD. While the method of water collection is flexible, knowing the depth at which the sample is collected is of utmost importance as the discrete pH data will be compared to glider-based pH measurements at depth.

Samples at each selected depth are collected in duplicate in borosilicate glass bottles, capped and preserved with 0.02% saturated mercuric chloride for laboratory analysis of pH, TA, and/or DIC (Wright-Fairbanks et al. 2020).

ACTIVE MISSION GUIDANCE

This section describes the best practices for piloting a glider during a mission to collect pH data. The glider's computer (Persistor) can receive new mission commands to run that can change the depth of inflections, add new GPS waypoints, and run many other commands. During the mission, it may be essential to change the flight path of the glider for efficient sampling and energy usage and/or to minimize biofouling. Efficient sampling requires the user to adjust the glider speed on the dive, so it is the same as the climb. In the Mid-Atlantic Bight (MAB), the speed of the glider is changed in one of two ways: Adjusting the buoyancy pump or changing the pitch angle to 22 instead of 26 degrees. In certain scenarios, users may need to turn off sensors with high energy usage at certain times to preserve the battery usage for the duration of the mission. During warmer seasons, it is also essential to coordinate sensor function and surface and/or dive times to reduce biofouling in the euphotic zone. This is achieved by reducing the

surface time used for the satellite modem to send sensor data back with Iridium. The Slocum Webb Glider G2 spends approximately 10-15 minutes at the surface while the Slocum Webb Glider G3 spends approximately 5-10 minutes at the surface. Gliders send a limited amount of data while at the surface (refer to Section VIII. B for more details about the file types with specified sensor data). Additionally, in past deployments in the MAB, the CTD pump was turned off at every surfacing for a minimum of 5 minutes to increase the dissolution and efficiency of biofouling agents. This allows the chemical substrate in the antifouling cartridge to increase in concentration around the pH sensor.

RECOVERY

As described in Section V. B., discrete water samples are collected at both deployment and recovery. The discrete seawater pH is compared to the glider's ISFET pH measurement at the closest depth on its last profile before recovery. The differences between the discrete pH and the glider pH are determined as ground-truthing offsets at each depth (i.e., sensor field accuracy).

DATA MANAGEMENT

A. Glider Data

Slocum gliders contain two built in processors, the flight processor, and the science processor. The flight processor is used for flight navigation and contains engineering sensor data such as pitch and battery life. The second processor controls integrated scientific instruments and logs scientific datasets from each instrument. The Slocum Glider Data File Primer Wiki Page (github.com/kerfoot/spt/wiki) describes the steps to renaming, decoding, and merging of glider data in preparation for processing. SPT toolbox has 2 core classes `Dbd` and `DbdGroup` that creates instances of native Slocum glider datafiles from 1 of 2 file types, `Dbd` and `.m/.dat`. Refer to the wiki page for a full description of the two file types.

B. Data Retrieval

Slocum gliders store all sensor data in six sets of files encoded from the dinkum binary data format: `dbd`, `ebd`, `sbd`, `tbd`, `mbd` and `nbd`. The six files can really be identified as three pairs, with one file in each pair storing data from the flight processor and the corresponding file in the pair storing data from the science processor. During glider missions only two (`sbd` and `tbd`) of the six binary data files can be sent to shore. These files contain a subset of the sensor data to reduce the file size and minimize the glider's surface time. Refer to the wiki page for more details about each binary file. At the end of the mission, the remaining binary files are transferred from the glider to the Dock Server.

C. Delayed Mode Preparation

Teledyne Webb Research provides utilities for renaming, decoding, filtering, and merging binary files into ascii files (human-readable format). A list of these utilities are available to subscribed users on the Teledyne Webb Research forum. An openly accessible shell script that simplifies these steps is also available on the Slocum Utilities (github.com/kerfoot/slocum). The first step is to rename the binary data files. The Slocum Glider Data File Primer Wiki Page (github.com/kerfoot/spt/wiki) provides a logical renaming convention (under Section 8.3 Renaming Files).

Next, the binary data file must be decoded to a readable format. At this stage, users may also opt to filter out unwanted sensors. This process is done individually on each file and differs based on whether the full file ascii header is contained in the file. A full description of filtering out sensor with no scientific data is available on the Slocum glider data wiki page.

For consistency, short, medium, and long binary files and their equivalents are loaded from the science processor into a single structure. This step can be done with TWRC utility which merges file pairs by timestamp. This creates a single merged file accepted by Dbd or DbdGroup class. A separate utility allows users to merge binary file pairs and produce a MATLAB file pair (.m & .dat) for processing in MATLAB. This method does not contain the default masterdata sensor units, so it is recommended to use the first method when creating instances of the Dbd or DbdGroup classes.

D. Copy Data to Centralized Location

To enable access to all team members, glider data sets are submitted to a central location using NOAA's Environmental Research Division Data Access Program (ERDDAP). ERDDAP allows team members to access gridded data through the web portal, data dissemination or a data distribution network. For a full list of this web services' capabilities visit the ERDDAP information page (<https://coastwatch.pfeg.noaa.gov/erddap/index.html>).

DELAYED MODE PROCESSING

A. Response Time Shift Corrections

This section describes the methods used to correct the thermal lag error for the Sea-Bird CTD which the ISFET based pH sensor is coupled with. This error stems from the mismatch between temperature measured outside the CTD's conductivity cell and conductivity measured inside the CTD's conductivity cell (Garau et al., 2011). The approach shown here refers to the relationship between a (amplitude of error) and T (time constant) (Morison et al.,

1994). This assumes that there is a constant flow through the CTD cell. This corrective approach calculates a time shift that produces the minimum area between glider profiles and applies a time shift to correct the error lag. It is assumed that each profile (consecutive up and down yo) corresponds to the same water mass. The area between the upcast and downcast defines one polygon and the perimeter. The MATLAB code uses sequential quadratic programming to find the minimum values of a constrained non-linear multivariate function. The minimum values represent the optimal time shift. The deployment-averaged time shift is applied to the full deployment. In some cases, where a clear shift in the ideal time shift during deployment is observed, different optimal time shifts are applied to the corresponding portions of the deployment [9, 10].

The minimization calculation is derived in MATLAB. This corrective procedure is similarly applied to the dissolved oxygen sensor observations. The minimization calculation is derived using MATLAB code and functions provided by the Slocum power tools toolbox (github.com/kerfoot/spt). The steps below describe the minimization calculation in MATLAB:

1. Load each sensor one at a time (i.e., pH reference voltage, dissolved oxygen).
2. Using a loop, determine the time shift by iterating through each profile in one second intervals.
3. For a high vertical resolution, bin data by depth (0.25 m x 0.25 m).
4. Convert the raw glider data into a data array using the function 'toArray'.
5. Eliminate the column corresponding to depth. This dimension is removed to convert the dataset into a 2-dimension (2D) data matrix. (Note: Parameter inputs for CO2SYS need to be in a 2D array.)
6. Save combined 2D data matrix and time series as a new dataset.
7. Store the minimum and maximum data values as a variable.
8. Using a loop, determine the minimum area between paired upcasts and downcasts. In most cases, the deployment-average time shift can be calculated by taking the mean of the optimal shifts for each profile. It is recommended to iterate through one-second intervals and save increments as a new variable.
9. Plot the distribution of time steps to visually verify mean time shift. Shifts that equal 0 should be noted from the plots because these indicate that there is no ideal time shift for that pair, and therefore should be removed before calculating the average deployment shift.

B. Applying Mean Time Shift

After the mean is established, it is applied to the entire dataset. First, the pH reference voltage 2D data matrix must be combined with the time series. In the code, the time shift is applied by subtracting the mean time shift from the uncorrected time steps. This will roughly remove the distance between glider dives, correcting the mismatch from thermal lag. Lastly, the shifted pH reference voltage is saved with the rest of the deployment data. Below is a description of the MATLAB code used to apply the time shift:

1. Apply the mean time shift, calculated from the previous step, to the full glider dataset. This is done by combining the pH reference voltage 2D data matrix and the time series with the calculated mean time shift. This will roughly remove the minimal distance between glider profiles by subtracting the mean time shift from the entire glider dataset.
2. Save the new 2D data matrix and time series as a new dataset.
3. Add sensor unit headers to the dataset.

C. QA/QC pH Data

This section describes methods in Quality Assurance/ Quality Control of Real Time Oceanographic Data (QARTOD) to flag pH data or remove instances that fail each test. Depending on the end goal, the user should determine if flagged data will be removed or corrected. A full description of methods is available in the QARTOD Manual for Real-Time Quality Control of pH Data. These tests were proposed by the International Oceanographic Data and Information Exchange (IODE) and adopted by the Intergovernmental Oceanographic Commission (IOC). Each test is numbered in ascending complexity and grouped based on the applicable utility (Figure 4). The first four tests (Group 1) are grouped as a requirement for all pH measurements collected for the U.S. IOOS. Group 2 tests (5-7) are strongly recommended for all pH data measurements. Group 3 tests (8-11) are suggested. Although the tests in Groups 2 and 3 are recommended/suggested, the utility of each test must be determined by the user's specific needs. The thresholds of the tests will also need to be determined by varying factors limited to the user's region.

IOOS QARTOD Tests

Group 1 (Required)	Test 1: Gap Test
	Test 2: Syntax Test
	Test 3: Location Test
	Test 4: Gross Range Test
Group 2 (Strongly Recommended)	Test 5: Climatological Test*
	Test 6: Spike Test
	Test 7: Range of Change Test*
	Test 8: Flat Line Test*
Group 3 (Suggested)	Test 9: Multi-Variate Test
	Test 10: Attenuated Signal Test
	Test 11: Neighbor Test
Test Utilized	

Figure 4. U. S. IOOS recommended QC tests for pH measurements in order of implementation. Modified after Table 3-2 in the Manual for Real-Time Quality Control of pH Data Version 1.0: A Guide to Quality Control and Quality Assurance of pH Data Observations.

For glider-based pH observations in the MAB, we conduct tests 1-4 and 6. The Gap Test (1) identifies data gaps greater than 1 hour and includes variables: reference voltage, pH, time-shifted reference voltage, time-shifted pH, dissolved oxygen concentration, time-shifted dissolved oxygen concentration, chlorophyll *a*, temperature, and salinity. The Syntax Test (2) checks that data contain the proper structure and syntax. The criterion for this test varies by the user's application. For gliders, the data stored within NetCDF files on ERDDAP servers meet the Syntax criterion defined in the QARTOD manual. The Location Test (3) verifies that the physical location of each data instance lies within the study area. The Gross Range Test (4) removes recorded pH values outside the acceptable range of measurement. The acceptable range varies by the sensor and user's region. The Spike Test (6)

flags data points that exceed the relative threshold of its nearby neighbors (the average of the 10 surrounding neighbors). In the MAB, the low threshold for pH was defined at 0.05 and the high threshold defined at 0.2.

In many cases, more sustained pH observations need to be taken in a region to define the local or regional variability, climatology, or pH interactions with other variables needed to conduct some of the recommended or suggested tests. From Group 2, only the Spike Test (6) has been implemented on the glider-based pH data (Wright-Fairbanks et al., 2020). Due to lack of previous pH observations in the MAB, tests 5, 7, and 9-11 were not performed in recent glider-based pH studies (Wright-Fairbanks et al. 2020), but should be considered in the future as observations increase.

D. pH Calculation

pH is calculated from the pH sensor's quality-controlled reference voltage, manufacturer-provided calibration coefficients, seawater temperature, salinity and pressure (Saba et al., 2019b). As described previously in Section III, the pressure model, reference potential and temperature coefficient change with each sensor and are provided by the manufacturer. The salinity is derived from conductivity, temperature and pressure values from the glider CTD using the Gibbs SeaWater (GSW) Oceanographic Toolbox of TEOS-10. These calculations are performed in MATLAB. A full description of the pH equation and the supplemental MATLAB code are available in Saba et al., 2019.

E. Deriving Total Alkalinity (Optional)

Total alkalinity (TA) in the global ocean co-varies strongly with salinity. Therefore, it is possible to estimate the value of TA using their linear correlation; however, these relationships can be location-dependent. Previous studies verify that the TA in the MAB correlates strongly with salinity [28, 29], but in some regions the TA is influenced by other complex biological and physical processes. Users must first determine if a strong salinity-TA relationship is present in their region. For the MAB, salinity-TA slope is derived from a combination of vessel-based datasets and discrete samples collected during glider deployments and recoveries [9, 10]. Glider-derived TA is calculated by applying the salinity-TA linear relationship to the glider-based salinity data.

F. Fully Resolving the CO₂ System (Optional)

It is widely accepted that the marine carbonate system can be fully resolved using two measured carbonate chemistry parameters along with temperature, salinity, and pressure (Pimenta & Grear, 2018). This glider sensor directly measures pH (and temperature, salinity, and pressure), but if robust conservative salinity-TA based

relationships are available in the sampling region (see Section IX. E.), you can use pH and TA as the two carbonate chemistry inputs in software programs such as CO2SYS to calculate other parameters of the carbonate system, including aragonite saturation state.

CO2SYS is currently the most common software used to calculate marine CO₂ system variables in MATLAB. The program accepts the input of glider calculated CO₂ system variables to compute the other system variables in the marine CO₂ system (Sharp et al., 2020). This calculation also depends on several thermodynamic constraints specific to the environmental conditions in the user's region and dissociation reactions in the seawater carbonate system. The constraints used during the missions in the MAB are described in Wright-Fairbanks et al., 2020.

Summary

This comprehensive best practices document can be used as an instructional guideline for the collection of high-quality pH data for a broad range of user groups. With the growing number of users utilizing the high-resolution data collection capabilities of gliders, it is critical to have a reference for quality control of glider-based pH data collected through ocean acidification or water quality monitoring efforts. In sharing this document with the wider scientific and ocean observing communities, users can more confidently apply these standard practices in their use of deep ISFET-based pH glider sensors to better understand the variability and drivers of ocean carbonate chemistry in marine ecosystems. Standardized protocols for collecting data are essential for reproducible data within a coordinated effort.

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