Developing a profiling glider pH sensor for high resolution coastal ocean acidification monitoring

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Abstract-Coastal and ocean acidification can alter ocean biogeochemistry, with ecological consequences that may result in economic and cultural losses. Yet few time series and highresolution measurements exist to track the existence and movement of water low in pH and/or carbonate saturation. Past acidification monitoring efforts have either low spatial resolution (mooring) or high cost and low temporal and spatial resolution (research cruises). Therefore, there is a critical need to deploy new, cost-effective technologies that can routinely provide high resolution water column data on regional scales in our coastal ocean. We developed the first integrated glider platform and sensor system for sampling pH in the water column of the coastal ocean. A Deep-Sea ISFET (Ion Sensitive Field Effect Transistor) pH sensor system was modified and integrated into a Slocum G2 glider and tested during a deployment in the Mid-Atlantic Bight. Measurements of pH exhibited a time lag that shifted during the deployment, but shifts were applied to correct pH. Glider pH and spectrophotometric pH measured in discrete water samples were in good agreement for some comparisons but not others, and those offsets were likely the result of delayed or incomplete conditioning (at deployment start) or mismatches due to water sampling techniques. Glider pH data along the cross-shelf transect revealed higher pH associated with the depth of chlorophyll and oxygen maximums and a warmer, saltier water mass. Lower pH occurred in bottom waters of the middle shelf and slope, and nearshore following a period of heavy precipitation. These results demonstrate the application of glider-based acidification monitoring in other coastal regions, providing the foundation of what could become a national acidification monitoring network.

Keywords—ocean acidification; glider; monitoring; Mid-Atlantic

I. INTRODUCTION

Ocean acidification (OA) has presented great research challenges and has significant societal ramifications that range from economic losses due to the decreased survival of commercially important organisms to the ecological consequences associated with altered ecosystems [1, 2]. Particular areas of the coastal ocean are more susceptible to sustained, large increases in carbon dioxide (CO₂), including those in upwelling zones [3, 4], bays [5], and areas with high riverine and/or eutrophication influence [6, 7]. Yet few observations exist to track upwelling and movement of low pH water.

Past ocean acidification monitoring efforts have been limited to surface buoys equipped with sensors that measure pH and/or pCO_2 (the concentration of CO_2 in seawater), flowthrough pCO_2 systems utilized by research vessels, and water column sampling during large field campaigns (e.g. U.S. Joint Ocean Global Flux Study, Bermuda Atlantic Time Series, Hawaiian Ocean Times Series) with low spatial resolution (mooring) or with high cost and low temporal resolution (research cruises). Few of these efforts include the U.S. continental shelves, commercially important coastal regions where finfish, lobster, and wild stocks of shellfish are present [3, 8, 9, 10].

The recent development of pH sensors for *in situ* measurements of seawater pH has resulted in a growing number of autonomous pH monitoring stations in the US [11, 12]. New

pH sensors that can withstand higher pressure (depth) show great value in monitoring coastal systems. A Deep-Sea ISFET (Ion Sensitive Field Effect Transistor) profiling pH sensor was recently developed by Monterey Bay Aquarium Research Institute (MBARI) and Honeywell and has been successful in collecting high quality data on a depth-profiling mooring [12, 13, 14]. This recent monitoring in the open and coastal ocean has shown that the pH varies greatly in time and space, reflecting complex circulation patterns that are likely due to the influence of low pH deep water through mixing and the intrusion of low pH fresh and/or estuarine water [15, 16, 17, 18]. Earlier, an innovative approach of combined in situ pumping and shipboard measurements of pCO_2 also demonstrated rapid spatial variations of the CO₂ system in the upwelling margin offshore Oregon, USA [8]. These fluctuations may lead to large ecological and economic impacts, thus reinforcing the need for reliable high-resolution monitoring of the full water column.

Significant improvements could be immediately achieved with the implementation of a real-time monitoring network that quantified the spatial location, duration, and transport of the low pH water in coastal regions [12, 19]. The spatial, temporal, and depth resolution achieved from Teledyne Webb Slocum glider data far exceeds that from traditional sampling from ships and moorings [20, 21]. These systems can sample in depths as shallow as 4 meters and as deep as 1000 meters and have been used in a broad range of challenging environments including near ice shelves in the Antarctic, beneath hurricanes and coastal storms, and on river dominated continental shelves. Recent calls for an international observational network for ocean acidification identified underwater gliders as a potential pH monitoring instrument that "could resolve shorter spacetime scale variability of the upper ocean" [12, 19]. A variety of sensors have successfully been mounted on Slocum gliders. To date however, no direct measurements of ocean pH have been collected by pH sensors mounted on these gliders.

We present here the recent development of the first integrated glider platform and sensor system for sampling pH in the water column of the coastal ocean on a regional scale. Specifically, we modified and integrated a deep rated version of the ISFET-based pH sensor, the Deep ISFET pH sensor system, into a Slocum G2 glider science bay. In addition to pH, the glider is equipped with sensors that will provide profiles of conductivity, temperature, depth, spectral backscatter, chlorophyll fluorescence, and dissolved oxygen (DO) to enable the mapping of ocean pH against the other variables. This new sensor suite was recently tested during a deployment in the Mid-Atlantic Bight (MAB), a highly productive wide and shallow continental shelf that undergoes seasonal upwelling events and is influenced by oceanic, riverine and estuarine inputs. The MAB is embedded in the U.S. Northeast Shelf (NES), one of the nation's most economically valuable fishing regions, but water column pH measurements are sorely lacking. Hence, the glider deployment presented here delivers a much-needed full characterization of water column pH dynamics in the MAB from the nearshore to the shelf-break and demonstrates the application of glider-based acidification monitoring in other coastal regions.

A. pH Sensor Integration

The Deep ISFET pH sensor was modified by Sea-Bird Scientific, and its integration into a Slocum Webb G2 glider (200 m) was a coordinated effort between Rutgers, Sea-Bird Scientific, and Teledyne Webb Research. To optimize the performance of the pH sensor for use on a glider. Sea-Bird Scientific significantly modified the original design of Deep ISFET pH sensor developed by MBARI [14]. Given the light sensitivity of the Deep ISFET and desire to be closely coupled with CTD (conductivity, temperature, depth) data acquisition, the Deep ISFET was reconfigured by Sea-Bird Scientific to fit into the existing rectangular glider CTD port utilizing a shared pumped system to pull seawater in past both the pH and CTD sensor elements (Fig. 1, top). Prior to integration with the glider CTD, the Deep ISFET pH sensor was calibrated in a custom temperature-controlled pressure vessel filled with 0.01 N HCl over the range of 5-35°C and 0-3000psi [14]. After the temperature and pressure calibration was completed, the Deep ISFET pH sensor was integrated with the glider CTD and conditioned in natural seawater for one week [14]. Teledyne Webb Research facilitated the integration of the new Deep ISFET pH/CTD unit into a standard glider science bay hull section. This standalone science bay was also outfitted with a WET Labs BB2FL ECO puck configured for simultaneous fluorescence, CDOM, and optical backscatter measurements, and complimented the existing Aanderaa optode integrated into the aft of the glider for measuring DO. Teledyne Webb Research environmentally cycled (pressure and temperature), bench tested, and performed in-water tests on the completed assembly prior to deployment. A proglet was written for the glider science processor to ingest, store, and make available the data at each surface interval. The resulting streamlined version utilizes the same mounting form factor as the SBE41CP pumped CTD, the standard model presently installed in Slocum gliders. This solution provides a backward compatibly to the existing fleet of Slocum gliders.

After the pre-deployment tests were completed, the science sensor bay was assembled into the glider (Fig. 1, bottom) and placed in a seawater tank at Rutgers University for one week at room temperature and pressure in order for the pH sensor to condition to the seawater off the coast of Atlantic City, New Jersey [14, 22]

B. Glider Deployment

After the sensor integration, factory calibration, testing, and conditioning was complete, we tested the capability of the glider sensor package on the MAB shelf. Slocum gliders operate by increasing and decreasing volume with a buoyancy pump to dive and climb in repeat sawtooth sampling patterns. Wings, a pitch battery, and the shape of the glider body result in forward motion with an aft rudder and internal compass maintaining a preprogrammed heading while underwater. At pre-programmed surface intervals the glider acquires new location information, downloads new mission parameters, and sends back real time data. The glider, RU30, used in this study was a coastal glider with a 200 m rated pump. Coastal gliders profile vertically at 10-15 cm s⁻¹ and travel horizontally at speeds of ~ 20 km day⁻¹.



Fig. 1. Deep ISFET pH sensor integration. Coupled pH and CTD integration into a standalone science bay (top), completely assembled in the glider (middle), and deployed in the Mid-Atlantic (bottom).

Science sensors sample at 0.5 Hz resulting in measurements at every 20-30 cm intervals vertically.

We deployed the glider on May 2, 2018 ~9 km off the coast of Atlantic City, NJ (17 m water depth) (Fig. 2). Upon deployment, we conducted a CTD hydrographic profile and several individual casts with a 5 L Niskin bottle to sample



Fig. 2. 3-dimensional depiction of calculated pH along the glider's crossshelf transects, May 2018. The glider was deployed off the coast of Atlantic City, New Jersey and took measurements of pH from nearshore to the continental shelf break (top), and back from the shelf break to shore (bottom).

discrete seawater samples for ground truthing the sensor (see below) after which, the glider was sent toward its next offshore waypoint to begin its cross-shelf transect. The glider completed a full cross-shelf transect in 20 days, and was recovered on May 22, 2018 ~24 km off the coast of Atlantic City, NJ (25 m water depth). The glider transmitted subsets of the data in real time and we downloaded full resolution datasets after recovery.

C. pH Data Analysis

pHtotal was calculated using the glider-measured reference voltage, pressure, sea water temperature, salinity, and sensorspecific calibration coefficients. The final equation used to calculate pH (below) was derived and modified from previous efforts [12, 14, 23, 24, 25]:

$$pH_{total} = \frac{\frac{V_{ref} - k_0 - k_2 * t - f(p)}{s_{nernst}} + \log(Cl_T) + 2 * \log(\gamma_{HCl})_{T,P} - \log\left(1 + \frac{s_T}{\kappa_{STP}}\right) - \log\left(\frac{1000 - 1.005 * S}{1000}\right)$$
(1)

Where:

$$S_{nernst} = \frac{R*T*\ln(10)}{F}$$
(2)

$$\log(\gamma_{HCl})_{T,P} = \log(\gamma_{HCl})_T + \left(\frac{V_{HCl}*p}{\ln(10)RT}\right)/2$$
(3)

R is the universal gas constant = 8.314472 J/(mol*K)t is the temperature in °C T is the temperature in K S is salinity in psu

P is the pressure in dbar

p is the pressure in bar

F is the Faraday constant = 96485.3415 C/mol

 k_0 is the cell standard potential offset

 k_2 is the cell standard temperature slope f(p) is the sensor pressure response function

Vref is the reference voltage

VHCl is the partial molar volume of HCl Cl_T is total chloride

 $(\gamma_{HCl})_T$ is the HCl activity coefficient at T

 $(\gamma_{HCl})_T^T p$ is the HCl activity coefficient at T and p

 S_T is total sulfide

KSTP is the Acid Dissociation Constant of HSO_{4,T&P}

Reference voltage and derived pH measurements exhibited a time lag during deployment (Fig. 3). To correct this lag, each data segment was run through iterations of time shifts from 0 seconds to 60 seconds to determine which shift minimized separation between the up and down profiles in the segment. The resulting matrix indicated two distinct time-shift zones, with the first 1/3 of deployment segments requiring a 47-second time shift (Fig. 3A) and the last 2/3 of deployment segments requiring a 25-second time shift on average (Fig. 3B). The change in time lag throughout the deployment may indicate a pH sensor conditioning period, wherein the sensor was acclimating to water conditions. Time lag can be corrected on an individual segment basis regardless, so the two shifts were applied to their respective segments in order to present time-corrected pH data.



Fig. 3. Example segments of uncorrected and corrected time lag observed in glider pH data. A 47-second lag was observed and corrected during the first third of the deployment (A), and a 25-second lag was observed and corrected in the last two thirds of the deployment (B). The time lag correction adjusted the measurements of pH reference voltage (left columns), and hence the calculations of pH (right columns).

D. Quality Assurance and Quality Control (QA/QC)

The hydrographic (CTD) and DO data collected during the glider missions follows the QA/QC procedures outlined in an approved EPA Quality Assurance Project Plan (QAPP) that was developed specifically for glider observations of DO along the New Jersey coast [26]. The procedures include pre- and post-deployment steps for each sensor to ensure data quality for each deployment. Beyond these common measurements, the science bay of the glider was outfitted with an ECO puck and the Deep ISFET profiling pH sensor. QA/QC procedures for each sensor are described in detail below.

<u>CTD</u>. The hydrographic data for each mission was sampled with a pumped CTD specifically engineered for this glider. Based on manufacturer specifications, the CTD was factory calibrated by SeaBird Scientific upon completion of the CTD-Deep ISFET integration. The QAPP requires a two-tier approach to verify the temperature and conductivity data from the glider CTD [26]. The first-tier test is a pre- and postdeployment verification between the glider CTD and a factory calibrated SeaBird-19 CTD in our ballast tank at Rutgers University in New Brunswick, NJ. The second-tier test is an *in situ* verification at both the deployment and recovery of the glider. For each deployment and recovery, we lowered a manufacturer calibrated SeaBird-19 CTD to compare to the concurrent glider profile. This second-tier test gives an *in situ* comparison within the hydrographic conditions of the mission.

<u>Aanderaa optode</u>. The DO data was sampled with an optical sensor unit manufactured by Aanderra Instruments called an optode. Like the CTD, we deployed a glider optode that is factory calibrated at least once per year. In addition to these annual calibrations, we also completed pre- and post-deployment verifications. To do this we compared optode observations to concurrent Winkler titrations of a sample at both 0% and 100% saturation. The verification for this deployment met the QAPP requirement that all optode measurements are within 5% saturation of the results of the Winkler titrations for both the 0% and 100% saturation samples [26].

<u>BB2FL ECO puck</u>. The puck we deployed was standard factory calibration from WET Labs (recommended every 1-2 years for pucks in gliders). Fluorescence data from the puck was verified during testing and deployments with simultaneously collected field samples for fluorescence.

Deep ISFET profiling pH sensor. We followed Best Practices for autonomous pH measurements with the DuraFET, including the recommended rigorous calibration and ground truthing procedure [14, 22, 27]. Using a 5 L Niskin bottle aboard the vessel during deployment and recovery, three replicate water samples were collected in close proximity to the glider from multiple depths (0.5 m, depth of thermocline, and 2 m from bottom; see Table 1). During this 1-2 hour sampling procedure, the glider sampled the water column in close proximity to the vessel. Water samples were collected for pH, dissolved inorganic carbon (DIC), and total alkalinity (TA) analysis from the Niskin bottle into 250 mL borosilicate glass bottles. Sampling involved overflow of seawater for at least one to two volumes, after which bottles were gently filled completely to avoid gas exchange with surrounding air. One ml of sample was removed to create a small headspace to allow for seawater expansion. The sample was then poisoned with 50 μ L of saturated mercuric chloride, sealed with a pre-greased glass stopper and rubber band, and stored in a cool, dark location until analysis at Cai's laboratory (University of Delaware). Discrete sample pH was measured spectrophotometrically using purified M-Cresol Purple purchased from R. Byrne at the University of South Florida [28, 29]. The accuracy of pH data was calibrated against Tris buffers [30, 31] purchased from Andrew Dickson at UCSD Scripps Institute of Oceanography. Cai's lab has built a spec-pH unit similar to the Dickson Lab [32]. TA titrations were performed using open cell Gran titration and Apollo Scitech TA titrator AS-ALK2 following previously described methods [33, 34, 35]. DIC was measured using an Apollo Scitech DIC analyzer AS-C3, which acidifies a small volume of seawater (1.0 mL) and quantifies the released CO₂ with a LI-7000 Non-Dispersive InfraRed analyzer [34, 35]. Precision of TA and DIC are better than $\pm 0.1\%$. Measurements of TA and DIC were quality controlled using CRMs obtained from Andrew Dickson at UCSD Scripps Institute of Oceanography. Final carbonate system parameters on the discrete water samples were calculated using CO2calc software [36] using the guidelines for input (analysis) and output (*in situ*) temperature [37], a total pH scale (mol/kg-SW), K1 and K2 constants [38] with refits [39], and the acidity constant of KHSO₄ in seawater [40]. These discrete

samples were compared to the glider Deep ISFET-derived pH measurements.

III. RESULTS AND DISCUSSION

A. Glider and Discrete Sample pH Comparisons

Preliminary data demonstrate good agreement between glider-pH and pH measured spectrophotometrically from discrete samples near the surface at glider deployment (May 2; pH difference ranged 0.001-0.002) and at depth during recovery (May 22; pH difference ranged 0.000-0.006) (Table 1). However, larger differences between the two pH measurements occurred at depth during deployment (pH difference ranged 0.045-0.086) and near the surface at recovery (pH difference ranged 0.050-0.055).

The higher pH discrepancies observed at depth during deployment may have been caused by delayed or incomplete conditioning as the sensor was conditioned in warmer, surface seawater in the laboratory test tank. This is also supported by the longer lag time observed in the early part of the deployment (Fig. 3A). Further analysis is being conducted to evaluate whether conditioning led to this potential offset. Additionally, water sampling techniques employed could have resulted in either depth differences between glider pH measurement and pH in discrete seawater samples from Niskin collection at depth. The Niskin sampling bottle used did not have a CTD attached. Instead, cable metered markings were relied upon to reach target depths, and currents or slack on the cable could have resulted in sampling at depths above the target causing mismatch between glider pH and spec pH measurements. Improvements in sampling techniques are now being employed during current and future pH glider missions, and will be evaluated on if they reduce or eliminate pH discrepancies between the

TABLE 1. Ground truthing comparison of glider pH data and Spec pH (spectrophotometric pH) analysis from discrete samples at glider deployment (May 2, 2018) and recovery (May 22, 2018). Water samples were retrieved from surface, thermocline, and bottom depths, preserved, sealed, and transported to the lab for analysis.

Date and Time (EST)	Depth (m)	Glider pH	Spec pH
May 2, 10:15	0.5	7.949	7.950
May 2, 10:18	0.5	7.949	7.947
May 2, 10:20	0.5	7.949	7.951
May 2, 10:34	11	7.976	7.890
May 2, 10:45	11	7.961	7.895
May 2, 10:52	11	7.946	7.895
May 2, 11:09	15	7.974	7.907
May 2, 11:15	15	7.974	7.929
May 2, 11:22	14	7.974	7.904
May 22, 09:48	0.5	7.982	8.037
May 22, 09:52	0.5	7.985	8.035
May 22, 10:02	9	7.973	7.997
May 22, 10:04	9	8.005	7.999
May 22, 10:12	23	7.983	7.983
May 22, 10:15	23	7.982	7.977

measurements. These improved efforts include using a CTD mounted on a rosette frame with multiple Niskin bottles to ensure sampling occurs at target depth and simultaneous measurements of salinity and temperature with each depth-specific sample collection.

pH discrepancies observed at the surface upon glider recovery were likely caused from higher spatial variability of pH in nearshore surface waters after a high precipitation event (Fig. 4). While water sampling was conducted in close proximity to the glider (within \sim 100m), it could have occurred far enough away that different patches were sampled by the two methods creating the offset in pH measurements. The water sampling protocol at glider deployment and recovery has been modified for future missions so that surface seawater collection occurs directly adjacent to the glider (within 2m).

B. pH dynamics

The pH range observed during this Spring deployment was 7.910 to 8.163. pH was frequently observed highest in subsurface waters and was associated with the depth of chlorophyll and oxygen maximums (Fig. 4). Higher pH values in the chlorophyll maximum throughout the transect ranged between 8.000 and 8.079. During primary production, photosynthesis increases pH due to the uptake of CO₂. So, while the observed association between pH and chlorophyll was not surprising, the ability to resolve the subsurface pH peak from the high-resolution vertical sampling with the glider provides a valuable perspective from which to not only evaluate concurrent vertical distributions of pelagic organisms, but also to put into context past pH monitoring efforts that mostly sample surface waters [41, 42, 43, 44, 45, 46]. Higher pH in offshore slope waters was also associated with a warmer, saltier water mass and suggests mixing processes could play a major role in driving pH dynamics on the shelf. During the deployment, the glider measured warmer water in the upper mixed layer on its return transect, depicting the strengthening of seasonal summer stratification in the upper mixed-layer due to incident solar radiation. These warm surface waters on the return transect were associated with increased pH values (Fig. 4).

The lowest pH typically occurred in bottom waters of the middle shelf and slope and nearshore following a period of heavy precipitation (Fig. 4). Lower pH values in the mid-shelf and slope bottom waters ranged between 7.910 and 8.020. Lower pH in mid-shelf bottom water occurred in the Cold Pool. remnant winter water in the Mid-Atlantic Bight centered between the 40 and 70m isobaths [47]. The Cold Pool is fed by Labrador Sea slope water and is isolated when vernal warming of the surface water sets up the seasonal thermocline. The annual formation of Cold Pool water means its carbonate chemistry should reflect near real-time increases in atmospheric CO₂ and pCO_2 in its Labrador source water which is weakly buffered and exhibits lower pH and aragonite saturation (Ω_{Arag}) [45]. Thus, the dominant drivers of low pH, as well as high dissolved inorganic carbon (DIC) and low Ω_{Arag} [43], in shelf bottom water were likely a combination of stratification, biological activity (i.e., higher respiration at depth), and the inflow of Labrador Sea slope water into the Cold Pool. Nearshore, lower pH was associated with lower salinity from freshwater input that was most substantial during a high period of precipitation near the end of the deployment, whereby 4.45 inches of rainfall was recorded at Atlantic City Marina, NJ, between May 12-22



Fig. 4. Complete cross-sections of variables measured by the glider throughout its deployment in May 2018. The glider's scientific instruments measure temperature, conductivity (used to calculate salinity), dissolved oxygen concentration, chlorophyll fluorescence, and pH reference voltage (used to calculate pH) from the surface waters to the ocean floor.

(https://www.njweather.org/data/daily/272; NJ Weather & Climate Network; Fig. 4). This storm event resulted in the freshening of the entire water column near shore (30 m; Fig. 4). River runoff has low pH from the equilibration with atmospheric CO₂ concentrations, and its zero salinity and low/zero alkalinity greatly reduces buffering capacity to offset changes in *p*CO₂ and contributes to low Ω_{Arag} [6, 48].

Large cross-shelf and vertical gradients in pH observed from the glider represent diverse dominant drivers: 1) Freshwater input nearshore, 2) Mixing of water masses in slope water, and 3) A combination of biological and physical drivers on the shelf. Thus, processes impacting the relative drivers likely drives both small- and large-scale variability in carbonate chemistry in the Mid-Atlantic. Both the horizontal and vertical gradients of pH observed were, at times, particularly sharp, and this new glider pH sensor suite demonstrated the ability to characterize these critical zones.

IV. SIGNIFICANCE

This new glider pH sensor suite has demonstrated its potential to: 1) Provide high resolution measurements of pH in a coastal region; 2) Determine natural variability that will provide a framework to better study organism response and design more realistic experiments; and 3) Identify and monitor high-risk areas that are more prone to periods of reduced pH and/or high pH variability to enable better management of essential habitats in future, more acidic oceans. The first glider deployment reported here provided data in habitats of commercially important fisheries in the U.S. Northeast Shelf, and allowed for the examination of temporal and spatial pH variability, the identification of areas and periods of lower pH water, better understanding of how mixing events and circulation impact pH across the shelf, and the creation of a baseline to track changes over time during future, scheduled deployments. Furthermore, the integration of simultaneous measurements from multiple sensors on the glider provides the ability to not only distinguish interactions between the physics, chemistry, and biology of the ecosystem, but also to conduct salinity- and temperature-based estimates of total alkalinity in order to derive carbonate saturation state (Ω), a measure of whether calcium carbonate will dissolve or form [33, 43, 49, 50]. As such, if made commercially available, this sensor suite could undoubtedly be integrated in the planned national glider network [51, 52, 53] to provide the foundation of what could become a national coastal ocean acidification monitoring network serving a wide range of users including academic and government scientists, monitoring programs including those conducted by OOI, IOOS, NOAA and EPA, water quality managers, and commercial fishing companies. Finally, data resulting from this project and future applications can help build and improve ecosystem models. A range of data assimilative modeling systems has matured rapidly over the last decade in the ocean science community. Many of these systems are being configured to assimilate glider data (temperature and salinity) (i.e., ROMs). The technology produced from this project will enable the development of coastal forecast models with the capability to predict the variability and trajectory of the low pH water.

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