

1.0 TITLE: Continuous water quality monitoring in Barnegat Bay

QUALITY ASSURANCE PROJECT PLAN

Prepared by James Vasslides, Barnegat Bay Partnership

Effective Date: March 1, 2017

Project Duration: Ongoing

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Donna Ringel, Quality Assurance Officer
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James Vasslides, Quality Assurance Officer
Barnegat Bay Partnership date

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3.0 QAPP DISTRIBUTION LIST:

Signed copies of this Quality Assurance Project Plan (QAPP) and all subsequent revisions will be sent to the following individuals by electronic mail:

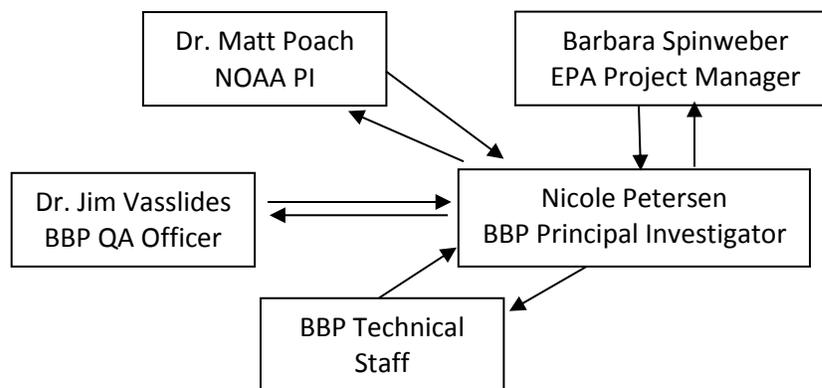
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4.0 PROJECT TASK ORGANIZATION:

Overall project management will be the responsibility of Ms. Nicole Petersen. Ms. Petersen will oversee the deployment and maintenance of the continuous water quality instruments and will be responsible for maintenance of the approved QA Project Plan. Dr. Jim Vasslides will provide quality assurance management, reviewing data acquisition and data analysis protocols, and ensuring compliance with all elements of the QA Project Plan. Dr. Matthew Poach will be responsible for the validation of pCO₂ data.

Organizational Chart-Lines of Communication



5.0 SPECIAL TRAINING/CERTIFICATIONS:

All staff conducting maintenance and calibration activities on the long-term continuous water quality datasondes will have successfully completed the web-based Exo University training program offered by YSI. This program will ensure a base level of knowledge in critical components of maintenance and calibration activities.

6.0 PROBLEM DEFINITION/BACKGROUND:

6.1 Problem Definition:

Coastal water quality impacts many commercial and recreational activities within the Barnegat Bay, including recreational and commercial fishing and shell fishing, swimming and ecotourism. These activities depend on a healthy ecosystem for their continued success. However, New Jersey's coastal waters are adversely impacted by a variety of stressors, potentially leading to decreased water quality, including algal blooms and low dissolved oxygen. To understand the impacts of these stressors on the water quality of Barnegat Bay it is necessary to collect water quality data at appropriate temporal and spatial resolution. The availability of continuous water quality data on a near real-time basis will provide environmental managers and researchers with a valuable tool for understanding estuarine processes and the impacts described above. Simultaneous measurement of parameters such as temperature, salinity, oxygen, pH, turbidity, and water level will allow correlations to be made between these parameters and meteorological conditions, tidal conditions and diurnal conditions. Real-time data collection eliminates the need for frequent trips to monitoring sites and benefits scientists and managers by allowing them to track environmental conditions at any given moment, more readily respond to episodic events as they happen which, in turn, can facilitate more accurate planning and decision making.

6.2 Background:

Monmouth University, with support from the Barnegat Bay Partnership (BBP) and others, has operated a suite of four continuous water quality monitoring stations in the Barnegat Bay since the mid-2000s (Bonnet Island, Barnegat Inlet, Seaside Park, Mantoloking/Point Pleasant Canal). The data generated from these stations was available through the Monmouth University website and was used by a variety of stakeholders. Monmouth University is no longer able to maintain and operate the previously deployed water quality stations. Therefore the BBP is taking over the maintenance and operation of three water quality monitoring stations.

7.0 PROJECT DESCRIPTION:

The objective of this project is to provide stakeholders (New Jersey residents, water quality managers and researchers) with timely access to measurements of coastal water quality. This will be done through the refurbishment of two existing long-term water quality monitoring stations (Seaside Park and Mantoloking) and the installation of a new station at Beach Haven (Table 1). Information to be provided at all stations will include: pH, turbidity, temperature, dissolved oxygen, salinity and water level. Additionally, the new Beach Haven station will measure pCO₂ to aid in understanding the impacts of coastal acidification. This information is expected to be useful to a wide range of users including fishermen, students, educators, researchers, and the general public. Persons interested in knowing the current conditions in "their bay" or estuary will find this valuable and should gain a better understanding of the dynamics of water quality in the waters near their home.

Site Name	Location	Waterbody	Latitude	Longitude
Mantoloking	Mantoloking Yacht Club	Barnegat Bay	40.0374 N	74.05405 W
Seaside Park	Seaside Park Yacht Club	Barnegat Bay	39.921813 N	74.0828445 W
Beach Haven	Morrison's Marina	Little Egg Harbor	39.567079 N	74.245045 W

The YSI Exo2 multiparameter data logger system is being used in this project. The YSI Exo2 multiparameter data logger system is designed for long term *in situ* monitoring and profiling. The Exo2 series data sonde uses a fully integrated sensor setup that accurately and reliably measures the parameters chosen: water temperature, conductivity, salinity, dissolved oxygen, pH, turbidity, and water level.

To accurately measure changes in water chemistry associated with coastal acidification, the Beach Haven station will also be equipped with a Satlantic SeaFet high precision pH sensor and a Pro-Oceanus CO₂-Pro CV CO₂ sensor. In combination with the data from the YSI Exo2 sensors we will be able to measure changes in pCO₂ concentration at the appropriate scale.

Each of the monitoring stations consists of one deployment platform that will be affixed to a bulkhead, piling or other dock structure and is assigned two YSI data sondes; one data sonde is deployed in the water and a second remains ready for a maintenance and calibration swap every 3 - 4 weeks. Prior to initial deployment, each of the YSI Exo2 data logger systems will be programmed to record temperature, salinity, dissolved oxygen, pH, turbidity, and water level every 15 minutes. The Satlantic and Pro-Oceanus sensors will also record data concurrent with the YSI. Each data

sonde removed or swapped from the field will subsequently be brought back to the laboratory for cleaning and calibration for redeployment. The Satlantic and Pro-Oceanus sensors are designed for long-term deployment, and will only be brought back from the field on an as-needed basis for cleaning and calibration (see Section 13.2 for additional details). Once deployed, the monitoring stations will remain operational as long as possible, with a goal of year round at most locations, but a minimum of early spring until late fall at each location.

The data is transmitted via a cellular modem once per hour to the New Jersey Department of Environmental Protection Bureau of Marine Water Monitoring, where it is downloaded and sent to their website for data retrieval by other organizations. As stated above, it is anticipated that data will be continuously collected between March and November annually.

8.0 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA:

Data quality objectives (DQOs) for the water quality parameters being measured can be expressed in terms of accuracy, precision, and completeness goals. These DQOs were established by obtaining estimates of the most likely data quality that is achievable by the instruments based on the instrument manufacturer's specifications.

The DQOs are used as quality control criteria for field measurements to set the bounds of acceptable measurement error. Generally speaking, DQO's are usually established for the following aspects of data quality: precision and accuracy, representativeness, comparability, and completeness.

8.1 Precision and Accuracy

The term accuracy is defined as the difference between a measured value and the true or expected value, and represents an estimate of systematic error or net bias. Precision is defined as the degree of mutual agreement among individual measurements, and represents an estimate of random error. Collectively, accuracy and precision can provide an estimate of the total error or uncertainty associated with an individual measured value.

Accuracy and precision will be managed by using calibrated YSI Exo2-series datasondes to collect water quality data at each of the sites. According to the manufacturer's recommendation, individual datasondes can remain deployed for a period of 3 -4 weeks and accurately provide reliable data. At the end of this time period, the datasondes in the field will be swapped out for a newly calibrated unit.

During deployment, transmitted data will be reviewed and tracked and any anomalies will be noted and investigated to confirm that the instrument is fully operational and providing credible data. If data being collected is suspect, the data sonde will be inspected and, if necessary, a newly calibrated unit will be deployed as soon as possible. Suspect readings include consistent reporting of dissolved oxygen levels indicating hypoxic conditions or super saturation, salinities above 32 parts per thousand, and pH levels below 5.0 or above 9.5.

The data quality objectives for the water quality parameters to be measured with the YSI Exo2 data logger system in the field are expressed separately as maximum allowable accuracy, precision and completeness goals in Table 2. The data quality objectives for the water quality parameters to be measured with the Pro-Oceanus CO2-Pro CV and Satlantic SeaFet are listed in Table 3.

Table 2: Data Quality Objectives for surface water quality measurement using the YSI Exo2 multi-parameter datasonde system			
Parameter	Accuracy Goal	Precision Goal	Completeness Goal
Dissolved oxygen	±0.3 mg/L	10%	100%
Salinity	±0.5 psu	10%	100%
pH	±0.3 units	10%	100%
Temperature	±0.5 °C	10%	100%
Turbidity	±0.3 FNU	10%	100%
Water Level	±0.06 ft, ±0.02 m	10%	100%

Table 3: Data Quality Objectives for surface water quality measurement using the Pro-Oceanus CO ₂ -Pro CV and Satlantic SeaFet (pH)			
Parameter	Accuracy Goal	Precision Goal	Completeness Goal
CO ₂	+/- 20 µatm	10%	100%
pH	+/- 0.04 units	10%	100%

Pre and Post calibration checks on known standards should be within the accuracy goal for each parameter for each device, and multiple readings at that time should fall within the precision goals. During deployment, accuracy of pH and pCO₂ readings will be checked periodically against values obtained from discrete sampling.

8.2 Bias

In order to eliminate bias, which could cause errors in data obtained during the project, all equipment will be inspected and properly calibrated as described in Section 13 of this QAPP before being deployed. Calibration of the datasondes will always be performed by the same trained personnel following detailed procedures. This reduces the likelihood of human (operator) induced error.

8.3 Representativeness

The concept of representativeness refers to the ability of the project to accurately and precisely characterize the existing conditions of a water body through the measurement of selected environmental parameters. In terms of the project sampling design, the sites of deployment have been selected to be as representative as possible of conditions in the water bodies at large where they are located taking into account location, accessibility and security. Additionally, this monitoring program is part of a larger effort to deploy continuous water quality datasondes in the bay, and thus should be looked at as part of a larger program. These sites were picked based on local knowledge and in consultation with other water quality monitoring organizations (Jacques Cousteau National Estuarine Research River and NJDEP Bureau of Marine Water Monitoring).

8.4 Comparability

Comparability is defined as the confidence with which one data set can be compared to another. To ensure data comparability in this project, we utilize the same model YSI data logger systems being deployed by other organizations in the state including NJDEP, USGS, and Rutgers University. All of these data will be shared among the agencies and organizations via the internet and these data sets will undergo periodic review, comparison, and analysis by the group.

Each of the three stations is using the same hardware and are setup, operated and maintained in the same way. The only exceptions are the high precision pH and CO₂ sensors at Beach Haven. The

data collected by these sensors is consistent with that of discrete sampling technology and other continuous sensors, and will be comparable to the findings in other locations.

8.5 Completeness

Completeness is defined as a measure of the amount of data collected during each field sampling event compared to the amount that was expected to be obtained under the conditions of measurement. We have established a completeness goal of 100% for the various parameters being measured. However, a loss of data collection capabilities (power supply issues) or data outside of the normal parameter range (potential biofouling or sensor drift) may not prevent the remaining data from being used, depending on the goals of the user.

8.6 Sensitivity

Sensitivity is essentially the lowest detection limit of the method or instrument for each of the parameters being measured. The sensitivity of the YSI Exo2 datasonde for the parameters being measured is summarized in Table 4, and the Pro-Oceanus and Satlantic Sensors in Table 5. Sensitivities for the analysis of dissolved inorganic carbon (DIC) and for pH of discrete samples at the NOAA laboratory at provided in Table 6.

Parameter	Range	Accuracy	Resolution
Dissolved oxygen	0 to 50 mg/l	@ 0 – 20 mg/l; greater of 1% of reading or +/- 0.1 mg/l @ 20 – 50 mg/l; 5% of reading	0.01 mg/l
Salinity	0 to 70 ppt	Greater of +/- 2% of the reading or 0.2 ppt	0.01 ppt
pH	0 to 14 units	+/- 0.2 units	0.01 units
Temperature	-5 to 50°C	+/- 0.2°C	0.001°C
Turbidity	0 to 4,000 FNU	+/- 2% or 0.3 FNU	0.01 FNU
Depth (non-vented)	0 to 33 ft., 10 m	±0.013 ft, ±0.004 m	0.001 ft, 0.001 m

Parameter	Range	Accuracy	Resolution
CO ₂	0-3000 ppm	+/- 0.5%	0.01ppm
pH	6.5 – 9.0 units	0.02 units	0.004 units

Parameter	Range	Accuracy	Resolution
DIC	0-3000 µg C	+/- 0.3%	< 1 µg C
pH	7.0 – 8.2 units	0.005 units	0.001 units

9.0 NON-DIRECT MEASUREMENTS (SECONDARY DATA):

Non-direct measurements (secondary data) will not be used as part of this monitoring project.

10.0 FIELD MONITORING REQUIREMENTS:

10.1 Monitoring Process Design

This project involves the reestablishment of two long-term continuous water quality monitoring stations and the establishment of a third station within the Barnegat Bay-Little Egg Harbor estuary complex (Table 1). These stations are part of a broader network of automated stations independently maintained and operated by the NJDEP, US Geological Survey, and JCNERR to assess changes in water quality within the Barnegat Bay-Little Egg Harbor watershed. The reestablished station locations were determined through cooperative discussion amongst all interested parties in an effort to provide continuous water quality data at reasonable spatial scales given budgetary constraints. The new station location, which includes the capabilities to measure changes in coastal acidification, was set by consensus among the interested parties considering the current monitoring coverage, the desire to place it near to sensitive biotic receptors (particularly shellfish), and limited suitable shore-side deployment locations.

Each of the stations will contain a YSI Exo2 multiparameter datasondes that will measure temperature, salinity, pH, dissolved oxygen, turbidity, and water level every 15 minutes. The Beach Haven station will also contain a Pro-Oceanus CO₂-Pro CV and Satlantic SeaFet that will measure CO₂ and pH, respectively, concurrently. All data will be stored on a datalogger and also transmitted hourly via cellular modem to the BBP for QA/QC and to an NJDEP website for public consumption. It is our intention to deploy the sensors from March to November of each year, with removal in the winter for annual regularly scheduled maintenance and to lessen the possibility of ice damage. We will attempt to extend the deployment of the devices through the winter, weather dependent.

10.2 Monitoring Methods:

Each station will include a multiparameter datasonde designed for long-term, *in-situ* monitoring. The YSI Exo2 datasondes will be equipped with sensors that measure and record the following surface water quality parameters: water temperature, salinity, dissolved oxygen, pH, turbidity, and water level. Each monitoring station will be assigned two YSI Exo2 datasondes: one datasonde is deployed in the water and a second remains ready for a maintenance and calibration swap every 3 - 4 weeks, depending on the degree of fouling. Each time a datasonde is replaced with a newly calibrated unit, the datasonde retrieved from the field is brought back to the BBP laboratory for post-deployment checks, cleaning, and maintenance. These retrieved units will subsequently be recalibrated prior to redeployment.

The Beach Haven station will also be equipped with a Pro-Oceanus CO₂-Pro CV and Satlantic SeaFet sondes. Both of these sondes are designed for long-term, *in situ* monitoring, and require annual calibration. However, during the YSI swap the housings will be examined for biofouling and cleaned as needed.

The datasondes will be located at each station in a manner that will allow for constant monitoring of surface water conditions at a depth of approximately one meter below the surface of the water. This will be achieved by hanging the data sondes inside PVC pipes affixed to the deployment platforms that have holes drilled in the lower portion of the deployment pipes along their length to allow for water exchange (see <https://www.ysi.com/File%20Library/Documents/Guides/Long-Term-Deployment-Tube-Guide.pdf> for an example and template). The deployment platforms will be constructed as fixed shore side locations on bulkheads/pilings at each site.

The YSI KORS software will be used to conduct the Exo2 sonde calibrations and setup. Once deployed, the Campbell CR1000 data logger and Data Management System will manage sensor sampling, data buffering and cellular telemetry to a base station. This system will be deployed shore-side adjacent to the data sonde platforms. The data sondes, water pump (Pro-Oceanus sonde only), and data loggers will be powered via an onsite 18v battery that is recharged through a solar charging system.

The Campbell CR1000 data logger systems will be programmed to record data every 15 minutes. The data telemetry system will provide data to the NJDEP web site in near real-time. The telemetry system is comprised of a field component located at each sampling site and an office component located at the NJDEP Bureau of Marine Water Monitoring. The field component consists of a housing, a data logger that stores the data collected by the sensors on the corresponding data sonde, a battery and solar panel to supply power, and a modem. Once an hour, the NJDEP computer server will connect with the data loggers located at each sampling site and will upload and update the data on the website.

Deployment and retrieval for the Exo2 data sondes will be conducted in accordance with the best management practices developed as part of the National Estuarine Research Reserve System(NERRS) System-Wide Monitoring Program (SWMP) YSI/Xylem EXO Multi-Parameter Water Quality Monitoring Standard Operating Procedure (Mensingher et al. 2016; Appendix 1). Post-deployment data downloads and processing will be conducted in a manner identical to those of the NJDEP and their approved QAPP to ensure consistency with other data collected within the bay.

10.3 Field Quality Control (QC):

Field quality control measures associated with deployment of continuous monitoring sondes can be divided into two categories; the physical environment of the sondes and the stability of the sensors.

Inspection and maintenance of the deployment platforms, data telemetry system, and associated power supply will be conducted with each site visit. Biofouling, which occurs when aquatic organisms such as algae begin to grow on the data sondes, can prevent the sensors from obtaining accurate readings. The Exo2 system is designed to operate in severe fouling environments and kept free of fouling by a universal anti-fouling sensor wiper assembly centrally installed on the sonde. In addition sensors are routinely wrapped in copper tape and the sonde guard is copper alloy. The PVC tubes holding the sondes are treated inside and out with antifouling paint every year. If biofouling is suspected of being an issue during deployments a cleaning brush will be used to clean the inside and a curved bladed long handled scrapper will be used on the outside of the tubes, which will be mounted to allow them to be rotated out of the water. These activities have been shown to be sufficient to overcome most of the problems associated with biofouling.

The sensors on the Exo2 units will be calibrated prior to deployment (section 13) and checked against known standards upon retrieval (Appendix 1, Section VI). Additionally, a YSI Pro-Plus Quatro handheld water quality meter will be used to collect discrete samples concurrent with the first and last sampling event of the continuous units as a field control.

The measurements from the Satlantic SeaFet will be checked against a discrete sample collected at initial deployment, weekly, and again at retrieval. Variance from the discrete sample will be documented in field records to be kept with the continuous data. If the variance between the discrete sample and the concurrent sensor reading exceeds the accuracy goal listed in Table 3, the sensor data will be flagged until a subsequent discrete/continuous sample pair read within the

accuracy range. This is in keeping with best practices, as is co-locating the sensor with a CO₂ and O₂ sensor (Martz, McLaughlin, and Weisberg 2015; Appendix 2).

11.0 ANALYTICAL REQUIREMENTS:

The analytical requirements are addressed throughout the QAPP and summarized in Tables 2 through 5. The specific methodology for each of the YSI sensors can be found in the Exo User's Manual (<https://www.yei.com/File%20Library/Documents/Manuals/EXO-User-Manual-Web.pdf>). The discrete water samples will be analyzed for DIC using a coulometer (UIC Inc.) and pH using a spectrophotometer (Varian) following the methods outlined in the Guide to Best Practices for Ocean CO₂ Measurements (Dickson et al., 2007). Sample analyses will be validated with certified seawater reference materials and tris buffers obtained from UC San Diego. The DIC and pH data along with in-situ sample temperature, pressure, and salinity will then be input to the CO₂SYs_xls program to calculate the in-situ pH and pCO₂ which will then be used to verify the continuous probe measurements (Perriot et al. 2006).

12.0 SAMPLE HANDLING AND CUSTODY REQUIREMENTS:

Sample collection and transport will be limited to discrete water samples collected to check against the SeaFet and CO₂-Pro sensors. These samples will be collected, preserved, and analyzed by NOAA personnel as part of their sampling protocol, and will be maintained within their custody throughout the process. Discrete samples will be collected following the methods in the Guide to Best Practices for Ocean CO₂ Measurements (Dickson et al., 2007). Briefly, discrete samples will be collected weekly at the probe measurement depth using a water sampling bottle and transferred to 300mL borosilicate glass bottles ensuring minimal interaction with the atmosphere. Samples will immediately be preserved with 0.06mL of a saturated mercuric chloride solution and transferred to the NOAA fisheries laboratory in Sandy Hook, NJ for analysis. Samples properly collected and preserved with mercuric chloride have a holding time greater than a month for both pH and DIC (Andrew Dickson, UCSD, personal communication).

All calibration records and field notes will be initialed, time and date notated and kept as part of the permanent project record.

13.0 TESTING, INSPECTION, MAINTENANCE, AND CALIBRATION REQUIREMENTS:

The YSI sensors require routine calibration checks to verify that their performance is within acceptable quality standards. The following sections will discuss the procedures and frequency for the various instrument calibrations that are key components in the collection of accurate environmental data.

13.1 Instrument/Equipment Testing, Inspection and Maintenance:

The Pro-Oceanus CO₂-Pro CV and the Satlantic SeaFet require annual maintenance and calibration verification to be performed by the manufacturers' representatives or service consultants. These procedures will be documented by date and the signature of the person performing the inspection, and the documentation will be maintained as part of the QA file.

For the YSI Exo2 sondes, an equipment testing, inspection, and maintenance log will be kept for each datasonde and updated prior to, and after each deployment.

13.2 Instrument/Equipment Calibration and Frequency:

An SOP has been developed and will be followed closely while maintaining, calibrating and operating the YSI Exo2 datasondes and associated equipment (Appendix 1). The methods utilized to calibrate the probes on the Exo2 datasondes are found in Appendix 1, Section II and will be used

prior to each deployment, while the post-deployment procedure in Section VI will occur following all deployments.

The Pro-Oceanus CO₂-Pro CV and the Satlantic SeaFet are factory calibrated based on conditions found at our deployment site, and will be returned to the factory each winter for inspection, repair, and recalibration.

13.3 Inspection/Acceptance of Supplies and Consumables:

The Project Manager and QA/QC Project Officer will be responsible for procurement of all supplies and equipment associated with the project covered by this QAPP. It will be their responsibility to inspect and accept all supplies and consumables received to ensure their quality and acceptability. All replacement probes for YSI datasondes must be received directly from the appropriate company. Probes will only be accepted if they are not noted as damages after a visual inspection, and pass initial calibration tests (YSI). Materials that do not meet this criteria will be returned to the manufacturer and replaced.

14.0 DATA MANAGEMENT:

As previously described, data collected at each of the monitoring sites will be transmitted via cellular modem to the NJDEP and BBP. Once an hour, the NJDEP computer server will connect with the data loggers located at each sampling site and will upload and update the data to the Bureau of Marine Monitoring website. The BBP system will also download the data hourly, but it will be stored for biweekly QA/QC checks to make a final archive for public use. This archived data will undergo a data review and validation process (see Section 16) prior to being made available to the public.

Transmitted data will be reviewed daily (excluding weekends) by the BBP via remote access to look for any anomalies, which will be noted and investigated to confirm that the instrument is fully operational and providing credible data. If data being collected is suspect, the datasonde will be inspected and, if necessary, a newly calibrated unit will be deployed as soon as possible. Suspect readings would include consistent reporting of dissolved oxygen levels indicating hypoxic conditions or super saturation, salinities above 32 parts per thousand, turbidity below 0.1 NTU or above 250 NTU, and pH levels below 5.0 or above 9.5.

YSI sensor calibrations are conducted using the YSI:KOR software. Station programming is accomplished through the Campbell datalogger software. Data QA/QC will be done using Microsoft Excel.

The hard copies of the datasonde calibration sheets and deployment logs will be held at the BBP office to enable QA/QC of the downloaded data, after which they will be stored by the BBP indefinitely.

15.0 ASSESSMENTS AND OVERSIGHT:

The BBP's QA/QC Project Officer will ensure that all data from the project are generated in accordance with procedures outlined in this Quality Assurance Project Plan. Other project participants will immediately report any problems or QA/QC issues to the QA/QC Project Officer. The QA/QC Project Officer will recommend appropriate corrective action and determine the acceptability of affected data. The BBP QA/QC Project Officer will conduct an audit of the calibration procedures, field deployment, data retrieval, and data verification within the first three months of the start of each sampling season.

The QA/QC officer will be present during the initial calibration and datasonde deployment each year to ensure consistency with previous years' efforts. They will also be tasked with ensuring that no unacceptable data (i.e., data that has previously been deemed suspect) is released or included in evaluations and analysis of results.

The QA/QC Project Officer shall keep a written record of any deviations from the approved QAPP. Results of all corrective actions will also be documented for the record.

16.0 DATA REVIEW, VERIFICATION, VALIDATION AND USABILITY:

16.1 Date Review, Verification, and Validation

Transmitted data will be reviewed daily and any anomalies will be noted and investigated to confirm that the instrument is fully operational and providing credible data. If data being collected is suspect, the data sonde will be inspected and, if necessary, a newly calibrated unit will be deployed as soon as possible.

Discrete sample analyses will be validated with certified seawater reference materials and tris buffers obtained from UC San Diego. Samples will only be analyzed when the reference materials produce results that meet the data quality objectives in Table 6.

Raw data is currently directly disseminated via the web. No flagging of suspect data is currently being provided in real time. The following disclaimer is posted on the web site:

Warning: You have chosen to graph Real-time Data. This data is preliminary and has yet to be QA'd. Use at your own risk.

Post processed data is examined for outliers, effects of drift, miss-calibration, and or sensor failure.

Manual Validation

Manual validation will take place twice, once before, and once after, the automated validation.

Data Screening: This process involves screening of the individual stations' real-time data files for each parameter measured for erroneous or unusual data. All suspect data is reviewed against environmental factors that may explain the values before being excluded from the dataset. All probe diagnostic values collected during the deployment will be evaluated to ensure the sensors were within the acceptable range and functioning properly; all data found to be collected with a malfunctioning probe will be deleted. All pre-deployment and post-deployment calibration and diagnostic values are evaluated to ensure proper function of sensors and to monitor for sensor drift during the deployment.

All data is compared to handheld field meter data collected at the time of deployment and at retrieval. The field meter data will be used to evaluate sensor accuracy and drift. This data will allow for the calculation for drift correction, if necessary.

All changes are made to a file copy representing the valid data. Original data before validation is stored in the data logger program file folder, unedited.

Pre and Post Deployment Sensor diagnostic Operating Range

Parameter	Range
Dissolved Oxygen Sensor (gain)	0.87-1.25
pH sensor Buffer 7 (mv)	0 +/- 50

pH sensor Buffer 4 (mv)	+180 +/-50
pH sensor Buffer 10 (mv)	-180 +/-50
Conductivity (cell constant)	0.469 +/- 0.05
Millivolt span between pH 4 and pH 7 Buffers	165 to 180
Millivolt span between pH 7 and pH 10 Buffers	165 to 180

Automated Validation

After the manual validation, the data files are run through an automated process to flag suspect data based on set threshold values.

Range Test: This process compares the value to a range expected set for each parameter. The range is based on historical data for estuarine waters.

Parameter	Validation Range
Chlorophyll a (ug/l)	0.1 to 365
Dissolved Oxygen (mg/l)	3 to 13
Dissolved Oxygen % saturation	50 to 300
pH	7 to 9
Salinity (ppt)	5 to 35
Specific Conductance (mS/cm)	10 to 52
Temperature (°C)	4.5 to 32
Turbidity (NTU)	0.1 to 250

Spiking test: This process compares the values to a unlikely interval difference, for each parameter for 15 minute intervals.

Parameter	Unlikely Interval Difference (15 minute interval)
Chlorophyll a (ug/l)	5
Dissolved Oxygen (mg/l)	2
Dissolved Oxygen % saturation	15
pH	0.25
Salinity (ppt)	2
Specific Conductance (mS/cm)	5
Temperature (°C)	1
Turbidity (NTU)	15

If a data record fails either Range or Spiking test, that record receives a comment that indicates the result seems to be “Low”, “High” or a “Big Jump”. These represent flagged markers and none of the data is deleted at this point in time.

The file containing all the data after the automated scan, including the flagged records marked for one of the above reasons, is carefully evaluated on whether the result is actually valid. This is done by comparing various ecological variables to determine whether natural events (excessive rainfall, droughts, etc.) have led to these flagged results. If it is determined that the data is valid, the flagged comment is removed and data is considered valid, otherwise, data will be removed permanently.

The post-processed data will eventually be to upload the data to the Rutgers University Continuous Monitoring Website.

16.2 Reconciliation with user requirements:

Users of the data collected will include collaborating agencies and organizations including the Barnegat Bay Partnership, NJDEP Bureau of Marine Water Monitoring, Stevens Institute, Monmouth County Board of Health, etc. In addition the data will be available to other interested scientists, agencies, and the public via the NJDEP Bureau of Marine Water Monitoring web site. However, it should be noted that in any use, the end user must evaluate the data using quality criteria appropriate for their intended use or decision-making process.

17.0 REPORTING, DOCUMENTS AND RECORDS:

All QAPP related data and all associated raw data records (including records of calibrations and calibration checks, deployment log books and other pertinent project related documents) will be maintained in electronic and hard copy at the Barnegat Bay Partnership’s offices at Ocean County College and shall reside indefinitely from date of collection. If Barnegat Bay Partnership can no longer provide the required storage, the data shall be transferred for archival storage to the NJDEP.

18.0 CORRECTIVE ACTIONS:

During deployment of the data sondes, transmitted data will be reviewed and tracked and any anomalies will be noted and investigated to confirm that the instrument is fully operational and providing credible data. If data being collected is suspect, the data sonde will be inspected and, if necessary, a newly calibrated unit will be deployed as soon as possible.

The post-deployment probe diagnostic values will be evaluated to ensure the sensors were within the acceptable range and functioning properly; all data found to be collected with a malfunctioning probe will be deleted from the corrected dataset. If a data record fails either Range or Spiking automated test, that record receives a comment that indicates the result seems to be “Low”, “High” or a “Big Jump”. These represent flagged markers and none of the data is deleted at this point in time.

The file containing all the data after the automated scan, including the flagged records marked for one of the above reasons, is carefully evaluated on whether the result is actually valid. This is done by comparing various ecological variables to determine whether natural events (excessive rainfall, droughts, etc.) have led to these flagged results. If it is determined that the data is valid, the flagged comment is removed and data is considered valid, otherwise, data will be removed permanently from the corrected file.

This QAPP will be reviewed every year for updates or changes. If updates or changes are necessary, all signatories will be requested to review and approve.

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APPENDICES:

Appendix 1. BBP EXO Multi-parameter Water Quality Monitoring Standard Operating Procedures

Appendix 2. Best Practices for autonomous measurement of seawater pH with the Honeywell Durafet pH sensor

Appendix 3. BBP Water Quality Calibration Log and Field Log

Barnegat Bay Partnership

Continuous Water Quality Monitoring Program

Standard Operating Procedure for the
Calibration and Maintenance of
YSI EXO-2 Multi-Parameter Data Sondes



Prepared By
Nicole Petersen
Barnegat Bay Partnership
March 2017

This procedure was developed specifically for The Barnegat Bay Partnership using best management practices for calibrating and maintaining continuous water quality monitoring data sondes developed by the following sources:

1. Mensinger, Mike (March 2016) National Estuarine Research Reserve System Wide Monitoring Program, YSI/Xylem EXO Multi-Parameter Water Quality Monitoring Standard Operating Procedure.
2. Schuster, Robert (December 2016) New Jersey Department of Environmental Protection Water Monitoring and Standards Bureau of Marine Water Monitoring Quality Assurance Project Plan for Continuous Water Quality Monitoring from Buoy's 2016.
3. EXO User Manual – Advanced Water Quality Monitoring Platform, www.exowater.com.

BACKGROUND:

Barnegat Bay Partnership's continuous water quality monitoring program consists of 3 monitoring stations in Barnegat Bay (Table 1).

Site Name	Location	Waterbody	Latitude	Longitude
Mantoloking	Mantoloking Yacht Club	Barnegat Bay	40.0374 N	74.05405 W
Seaside Park	Seaside Park Yacht Club	Barnegat Bay	39.921813 N	74.0828445 W
Beach Haven	Morrison's Marina	Little Egg Harbor	39.567079 N	74.245045 W

Each of the monitoring stations consists of one deployment platform affixed to a bulkhead, piling or other dock structure and is assigned two YSI data sondes; one data sonde is deployed in the water and a second remains ready for a maintenance and calibration swap every 2 - 4 weeks. Each of the YSI Exo2 data logger systems is programmed to record temperature, salinity, dissolved oxygen, pH, turbidity, and water level every 15 minutes. The raw data is transmitted via a cellular modem once per hour to the New Jersey Department of Environmental Protection Bureau of Marine Water Monitoring, where it is downloaded, processed and sent to their website for data retrieval by other organizations. This SOP will provide step by step instructions on how to connect to, calibrate, maintain and store the YSI EXO-2 multi-parameter datasondes for the Continuous Water Quality Monitoring Program. The consistent and accurate calibration and care of these sondes is crucial to reliable and useful data.

1.0 EXO COMMUNICATION & KORS SOFTWARE – CONNECTING THE EXO TO A PC OR LAPTOP

A copy of KORS software, (as of 3/08/2017, Version 1.0.12) is currently downloaded on the BBP's laptop and tech desk PC. This software is used for EXO communication, calibration, post-deployment readings, data file download, sonde/probe firmware updates, and any other necessary interaction with the sonde via a PC. The EXOwater.com website should be checked for software updates routinely. This section briefly covers how to connect the EXO2 sonde using KORS.

1.1 Sonde Connectivity:

EXO sondes are accessed via one of two potential options:

1. USB/SOA (Signal Output Adapter) Cabled Connection
 - a. Open KORS Software
 - b. Connect the USB cable to the PC and the blue SOA adapter to the sonde connector located on the top of the sonde.
 - c. Click the "Circular Blue/Green Arrows" icon (7th icon from the left in KORS)
 - d. Click Rescan
 - e. Click the COMM port that has the EXO USB adapter and EXO sonde ID shown
 - f. Click "Connect"
 - g. If the USB adapter or sonde do not show up at first, unplug the USB cable from the computer, plug it in again, and repeat steps c through f. If this fails to show the sonde, unplug the adapter from the sonde, re-connect the adapter, and repeat steps c through f.
2. Wireless Bluetooth Connection
 - a. Open KORS Software
 - b. Place the magnetized section of the black probe removal tool over the magnet icon located on the sonde (about halfway down the sonde within the black stickered area that says EXO2) to activate the sonde.
 - c. Click the "Circular Blue/Green Arrows" icon (7th icon from the left in KORS)
 - d. Click Rescan
 - e. Click the EXO sonde ID shown
 - f. Click "Connect"

NOTE: make sure to connect to the appropriate EXO sonde as the Bluetooth may pick up other active EXO sondes nearby.

2.0 RECORD KEEPING

A "BBP Continuous Water Quality Monitoring Calibration and Field Log" (BBP CWQM log) must be completed for each instrument's calibration, deployment, retrieval, and post-calibration procedures. These logs will be stored at the BBP in the binder labeled "CWQM – Sites/Calibration logs". Blank logs are stored on the shared drive under "continuous water quality monitoring/calibration/calibration logs". In addition, any field maintenance that is performed during an instruments deployment will be recorded on the log.

Prior to calibration, record the serial number for the sonde and each probe. To do this, perform the following while the sonde is connected to KORS:

1. Click the Gear Icon
2. Click Firmware

3. At this time check that all firmware and OS are up to date on this same page. Update if necessary.
4. Print this screen and store in the calibration binder (the user can double check accuracy of the serial number during calibration of each parameter).

3.0 CALIBRATION AND MAINTENANCE PROCEDURES

3.0.1 Calibration Frequency:

November through March - every 4 weeks

April through October - every two weeks

These are general guidelines. Probe drift, malfunction or increased/decreased biofouling may necessitate more or less frequent cleaning and calibrations.

3.0.2 Anti-fouling measures:

Biofouling presents challenges to the collection of accurate and reliable data. The following anti-fouling measures will be taken for ALL BBP sensors, probes and equipment prior to calibration and deployment.

1. Antifouling paint will be applied to all PVC that house sensors. YSI recommendations for tube construction are available at the following link: <https://www.ysi.com/File%20Library/Documents/Guides/Long-Term-Deployment-Tube-Guide.pdf>
2. Copper Sensor Guard – a copper alloy sensor guard offers biofouling properties and replaces the normal black plastic sensor guard. These are available through YSI.
3. Duct tape – will be applied to the sonde body to both reduce biofouling and aid in its removal.
4. Packing tape – will be applied beneath the duct tape for cleaner removal of tape.
5. Copper Tape - will be applied to the bodies of all sensor probes. This adhesive-backed tape, sold by YSI and other vendors, reduces biofouling when applied to the body of each probe. Sensor faces/caps should not be covered with copper tape.
6. C-Spray - while it does not prevent fouling, this spray material can be applied to the sonde connector region, sensors, and internal sensor guard faces to make biofouling removal easier (available through YSI, SKU616290).

3.0.3 How to install probes on the EXO:

1. Please refer to the EXO User Manual located on the shared drive or at www.EXOwater.com and the instructions that come with each new probe for complete probe installation instructions.
2. Order of installation: - Can be found on the firmware page as well
 - Port 1 - Turbidity
 - Port 2 – Optical DO
 - Port 3 – Empty – make sure to use a port plug
 - Port 4 – Wiped Conductivity/Temperature
 - Port 5 – pH

Port 6 – Empty – make sure to use a port plug
Port 7 –Central Wiper

3.0.4 General Calibration Considerations:

The following guidelines should be followed to insure proper laboratory practices, quality control and safety.

1. Please refer to MSDS sheets when handling any standard and follow recommended safety practices.
2. Lot numbers on all standards are to be recorded in the KORS software. Expired standards are to be discarded appropriately. Record the date a standard is opened on all standard bottles. Discard opened standards after 6 months. Turbidity standards are the exception; they should be discarded after 12 months of opening.
3. Make sure all equipment and work spaces are clean and dry before calibration.
4. All equipment and analyzers should be visually inspected for any abnormalities, such as a broken probe or damaged bulkhead.
5. Calibrations are best performed using a guard and calibration cup that are dedicated to calibration only and never taken in the field. This insures there is no contamination during the calibration process.
6. During the calibration **NEVER** accept any calibrations that display an error message. Troubleshoot the cause of the problem, correct it, and recalibrate or replace the probe before deploying the instrument.
7. Recommended probe calibration order: Temperature (not a true calibration, but a check against another source), Specific Conductivity, pH, Depth, Turbidity, Dissolved Oxygen.
8. Remove the Wiper Brush from the sonde before calibrations. The brush can trap residual standard and affect the calibration accuracy.
9. All diagnostic parameters (pH millivolts, pH slope, DO gain, and conductivity cell constant) for EXO sondes are presented after calibration of the respective parameter on the KORS generated calibration log sheet and should be printed and recorded on the BBP CWQM Log once each calibration is complete.

3.0.5 Calibration Supplies:

250ml plastic graduated cups

Compressed air

Kimwipes

Turbidity standard (see how to prepare a dilution if preparing this standard)

pH buffers (4,7,10)

Conductivity standard

YSI ProPlus handheld

Dedicated calibration cup and guard

CLEAN 5 gallon bucket

Air pump and air stone

Distilled water and rinse water bottle

Laptop with KORS software
EXO2 Datasonde
SOA/USB for sonde to laptop connection

The following sections provide step-by-step methods for the calibration of each probe type. All data is recorded on the BBP CWQM Log under Pre-Deployment Calibration.

3.1 Temperature Sensor Check:

While it is not possible to calibrate the temperature probe, a temperature test is performed to verify that the temperature probe is working properly. Using one of the two YSI ProPlus handhelds, perform the procedure below. BBP's two ProPlus meters are calibrated and maintained by DEP bureau of Marine Water Monitoring. The ProPlus is checked against a NIST traceable thermometer at the Bureau's Leeds Point laboratory. The correction factor of this meter is recorded on the unit with masking tape and may be verified by the calibration logs for each meter.

1. Allow the sonde and YSI ProPlus to simultaneously sit in an aerated 5 gallon bucket of room temperature tap water for at least 5 minutes to reach temperature equilibrium.
2. Connect to the sonde via KORS software.
3. Click the Green Running Man icon to place sonde into discrete mode.
4. Verify temperature readings have stabilized and record the sonde's temperature value in the Pre-Deployment section of the data sheet in the "Before Cal" field for temperature.
5. Record the DEP **corrected** temperature reading from the YSI ProPlus in the data sheet's Pre-Deployment "Standards" column.
6. Record the correction factor for the EXO sonde.
7. Remove the sonde from the water bucket

3.2 Specific Conductance Functional Test

The Specific Conductivity check will verify that cleaned and dry electrodes read $< 2 \mu\text{s/cm}$ with the probe dry and in air.

1. Rinse the Specific Conductance probe with Distilled Water after the temperature verification test.
2. Using a compressed air source, (Dust Off) blow the open channels and then carefully dry with a Kimwipe.
3. The Specific Conductance reading in air must be $< 2 \mu\text{s/cm}$, if greater than $2 \mu\text{s/cm}$ contact Xylem/YSI for assistance.
4. This reading is taken in discreet mode under the running man icon.
5. Record the Specific Conductance test value in the Comments section under Pre-Deployment calibration.

3.3 Conductivity Probe (Specific Conductivity & Salinity)

1 Point Calibration

1. Fill a clean EXO calibration cup with a small amount of rinse conductivity calibration standard (rinse standard is the term for calibration standard used during the previous calibration. Its use reduces cost and standard consumption).
2. Place the sonde with clean guard installed into the EXO calibration cup, tighten and shake to rinse the guard and probes.
3. Remove calibration cup from sonde keeping guard attached and empty out the rinse standard.
4. Repeat the above process 1-2 more times (YSI recommends rinsing a total of three times).
5. Fill calibration cup to the second line with new/unused conductivity calibration standard.
6. Place the EXO sonde into the calibration cup and tighten.
7. Click the calibration icon in KORS.
8. Click "Conductivity"
9. Click "SpCond" (Specific Conductivity)
10. Choose 1 point calibration and make sure the calibration standard value shows up properly (this may be entered manually each time or can be set to show up automatically by clicking the Gears icon, Calibration submenu icon, Cond icon, SpCond icon, and then entering the standard value for Cal Point 1, followed by clicking apply).
11. Type in the standard type, manufacturer, and lot # of the standard (standard type and manufacturer can be entered manually each time or auto-set using the procedure described in the previous step). Record the standard value in the "standards" column.
12. Click "Start Cal"
13. Once the temperature value has stabilized and "unstable data" in red font changes to "stable data" in green font, click "apply".
14. Verify the "Pending (Post) value is correct and click "Complete".
15. The calibration worksheet for the probe will pop up and the user should record the following three values:
 - a. Pre Calibration Value: record this value in the data sheet's "Before Cal" column.
 - b. Post Calibration Value: record this value in the data sheet's "Calibrated" column.
 - c. Cell Constant: record this value in the data sheet's "Sensor Diagnostics/Pre-Deployment" cell constant field. Review the cell constant value to make sure it is within the proper range of 0.5 +/- 0.1 for the Wiped CT sensor.
16. Print the calibration worksheet.
17. Close the calibration worksheet.
18. Pour the used standard into a container labeled "rinse" as this standard can be used as a rinse in a future calibration.

YSI Tips:

Never calibrate with a standard less than 1.0 $\mu\text{S}/\text{cm}$ as they are easily contaminated by residual Distilled water and electrical noise. Typical calibration errors are attributed to incorrect standard value input, inadequate calibration standard volume in the EXO calibration cup, or air bubbles in the conductivity cell.

3.4 pH Probe:

3 Point Calibration (pH7, pH10, pH4)

Note: All pH sensors require periodic reconditioning and cleaning, the pH reconditioning procedure should be performed quarterly and at the beginning of a new season.

3.4.1 pH7

1. Rinse the EXO calibration cup, guard, and probes with Distilled water to remove standard from the previous calibration.
2. Fill EXO calibration cup with a small amount of rinse pH7 calibration standard (rinse standard is the term for calibration standard used during the previous calibration. Its use reduces cost and standard consumption).
3. Place the sonde with guard installed into the EXO calibration cup and shake to rinse the guard and probes.
4. Empty out the rinse standard.
5. Repeat the above process 1-2 more times (YSI recommends rinsing a total of three times).
6. Place the sonde on the work bench with the guard removed.
7. Click the Green Running Man icon to run the sonde in discrete mode to get an air temperature reading. Once the temperature has stabilized, use that value to determine the exact values to input for your calibration standards. The standards will have pH values at various temperatures or ranges listed on the container.
8. Write the temperature compensated pH values in the data sheet's Pre-Deployment "Standards" column for the three standards to be used.
9. Fill calibration cup to the first line with the first pH calibration standard (pH7).
10. Click the calibration icon.
11. Click "pH".
12. Choose 3 point calibration and enter the pH7, pH10 and pH4 standard values determined in the previous Step. It is critical to note that unlike all other parameters; the exact pH value used for calibration may change slightly based on the air temperature at which you are calibrating. If the standard values shown in the calibration page have been auto-set and do not match the values you want, simply input the correct values and proceed to the next step.
13. Enter the standard type, manufacturer, and lot # for each calibration point.
14. Click "Start Cal"
15. Once the temperature value has stabilized and "unstable data" in red font changes to "stable data" in green font, click "apply".

16. Verify the "Pending (Post) value is correct and click "Proceed".
17. Pour the used standard into a container labeled "rinse" as this standard can be used as a rinse later.

3.4.2 pH10

1. Rinse the EXO calibration cup, guard, and probes with Distilled water to remove pH7 standard from the first part of the calibration.
2. Fill the EXO calibration cup with a small amount of rinse pH10 calibration standard.
3. Place the EXO sonde with guard installed into the EXO calibration cup and shake to rinse the guard and probes.
4. Empty out the rinse standard.
5. Repeat the above process 1-2 more times (YSI recommends rinsing a total of three times)
6. Fill the calibration cup with the next pH calibration standard (pH10).
7. Click "OK" when the small window pops up saying "Proceed to Standard (10.00 pH).
8. Once the temperature value has stabilized and "unstable data" in red font changes to "stable data" in green font, click "apply".
9. Verify the "Pending (Post) value is correct and click "Proceed"
10. Pour the used standard into a container labeled "rinse" as this standard can be used as a rinse later.
11. Rinse the EXO calibration cup, guard, and probes with Distilled water to remove pH10 standard from the first part of the calibration.

3.4.3 pH4

1. Fill the EXO calibration cup with a small amount of rinse pH4 calibration standard
2. Place the EXO sonde with guard installed into the EXO calibration cup and shake to rinse the guard and probes.
3. Empty out the rinse standard.
4. Repeat the above process 1-2 more times (YSI recommends rinsing a total of three times).
5. Fill the calibration cup with the next pH calibration standard (pH4).
6. Click "OK" when the small window pops up saying "Proceed to Standard (4.00 pH).
7. Once the temperature value has stabilized and "unstable data" in red font changes to "stable data" in green font, click "apply".
8. Verify the "Pending (Post) value is correct and click "complete".
9. The calibration worksheet for the probe will pop up and the user should record the following values:
 - a. Pre Calibration Value for Cal Point 1: record this value in the data sheet's "Before Cal" column.
 - b. Post Calibration Value for Cal Point 1: record this value in the data sheet's "Calibrated" column.
 - c. Raw Value pH mV: record in the data sheet's "Sensor Diagnostics/Pre-Deployment" pHX millivolts field.

- d. Record the values (Pre Calibration Value, Post Calibration Value, and Raw Value) on the data sheet for the 2nd and 3rd calibration points.
 - e. Also record the pH probe slope in the data sheet's "Sensor Diagnostics/Pre-Deployment" next to the text "calculated pH slope".
 - i. Verify that the pH slope is within the ideal range of 160 – 180. pH data collected with a probe slope of less than 155 requires mandatory coding as suspect data. It is not recommended to deploy a sonde displaying a pH slope at or below 155. A brand new pH probe will display a slope at or near 180. A probe displaying a slope of 160-165 indicates the probe tip is nearing the end of its lifespan and will require replacement in the near future.
10. Print the calibration worksheet.
 11. Close the calibration worksheet.
 12. Pour the used standard into a container labeled "rinse" as this standard can be used as a rinse later.

YSI Tips: pH probe tips typically last 1 – 1.5 years on average. The entire probe does not need to be replaced when its lifespan has ended; only the probe tip (Part #599795-02).

3.5 Depth/Water Level:

To be performed onsite at deployment.

1 Point Calibration

1. Fill EXO calibration cup with a small amount of water (the volume should not reach anywhere near the probes) to create a water-saturated air environment.
2. Screw the guard onto the sonde and place it into the calibration cup.
3. Allow the sonde to remain in a vertical position.
4. Click the calibration icon.
5. Click "Depth"
6. Click "Depth m"
7. Determine barometric pressure value in mmHG from one of the BBP's YSI ProPlus handhelds and record it in the "Pre-Deployment" "Before Cal" column inside the field next to "Baro Pres. (Depth Calib).
8. Click "Start Cal"
9. Once the depth value has stabilized and "unstable data" in red font changes to "stable data" in green font, click "apply".
10. Click "Complete"
11. The calibration worksheet for the probe will pop up and the user should record the following values:
 - a. Pre Calibration Value: record this value in the data sheet's "Before Cal" column for depth.
 - b. Post Calibration Value: record this value in the data sheet's "Calibrated" column for depth.

12. Close the calibration worksheet.
13. When you have returned to the office, you must print the calibration worksheet for the depth calibration.
 - a. In KORS, click the Data icon (file folder).
 - b. Click View Calibration Worksheets
 - c. Select Depth in the "Available Calibration Types" pull down.
 - d. Highlight the correct calibration by date, and click OK
 - e. When the worksheet opens, click Print and choose the appropriate printer and click OK. Once printed, close the calibration worksheet.

YSI Tip: Make sure the correct latitude has been entered into the EXO sonde.

3.6 Turbidity probe:

3.6.1 *Turbidity Probe calibration considerations:*

1. NTU (nephelometric turbidity units) and FNU (formazin nephelometric units) are considered synonymous for the purposes of this document.
2. Do not calibrate turbidity in the field as clean surfaces and solutions are essential for a good turbidity calibration.
3. Use the EXO calibration cup for turbidity probe calibration; do not use any other calibration vessel.
4. Bubbles over the optics will interfere with calibration therefore it is recommended to carefully pour standards into the calibration cup with the cup held at an angle to avoid aeration and to visually confirm all air bubbles are clear from the probe face before calibration.
5. A 2-point calibration can be performed when sensor drift is evident. In such a case a dilution of stock formazin standard may be used as a second point. Using distilled water as a 0 ntu calibration point is not recommended as any contamination from the calibration cup, guard or sensors may introduce error. For more on turbidity visit YSI's website.

3.6.2 *1-point Turbidity Probe calibration:*

1. Rinse the EXO calibration cup, guard, and probes with DISTILLED water to remove standard from the previous calibration.
2. Fill EXO calibration cup with a small amount of DISTILLED water. DISTILLED water serves as a rinse in this calibration.
3. Place the sonde with guard installed into the EXO calibration cup and shake to rinse the guard and probes.
4. Empty out the DISTILLED rinse water
5. Repeat the above process 1-2 more times (YSI recommends rinsing a total of three times).
6. Fill EXO calibration cup with a small amount of 126 FNU rinse standard.

7. Place the EXO sonde with guard installed into the EXO calibration cup and shake to rinse the guard and probes.
8. Empty out the 126 rinse standard.
9. Repeat the above process 1-2 more times (YSI recommends rinsing a total of three times).
10. Fill the EXO calibration cup to slightly above the first line with new/unused 124 FNU calibration standard by holding the calibration cup at an angle and slowly pouring the standard into the cal cup to avoid introducing air bubbles.
11. Place the EXO sonde with guard installed into the calibration cup; do this slowly to avoid generating air bubbles.
12. Gently tap the EXO sonde and calibration cup on the work bench at a 45 degree angle to insure air bubbles are not present on the sensor face. Visually inspect to make sure the probe face is air bubble-free before proceeding.
13. Click the calibration icon.
14. Click "Turbidity"
15. Click "Turbidity FNU"
16. Choose 1 point calibration and make sure the calibration standard shows up properly (this can be set by clicking the Gears icon, Calibration submenu icon, Turb icon, and then entering 124.00 for Cal Point 1 followed by clicking apply).
17. Enter the standard type, manufacturer, and lot #.
18. Click "Start Cal"
19. Once the temperature value has stabilized and "unstable data" in red font changes to "stable data" in green font, click "apply".
20. Verify the "Pending (Post) value is correct and click "Complete".
21. The calibration worksheet for the probe will pop up and the user should record the following two values:
 - a. Pre Calibration Value: record this value in the data sheet's "Before Cal" column.
 - b. Post Calibration Value: record this value in the data sheet's "Calibrated" column.
22. Print the calibration worksheet.
23. Close the calibration worksheet.
24. Pour the used standard into a container labeled "rinse" as this standard can be used as a rinse later.

NOTE: If preparing a 100 NTU solution as described in section 8.0, replace the 124 FNU value in the preceding steps with the 100 NTU standard value.

YSI Tips:

Take care not to touch, bang or scratch the turbidity probe as this can damage the optics and produce inaccurate readings. If necessary, the face can be gently wiped with a lint free Kimwipe to remove dirt or smudges.

3.7 Dissolved Oxygen Probe:

1 point calibration

1. Aerate a 5 gallon bucket filled $\frac{3}{4}$ full with tap water for at least an hour prior to calibrating a dissolved oxygen probe. This creates an air-saturated environment referred to as a 100% air-saturated water bath.
2. Place the EXO sonde into the bucket for 15-20 minutes before calibrating the DO probe in order to achieve temperature probe stabilization. Do not allow air bubbles to flow directly towards the DO probe's face.
3. Click the calibration icon.
4. Click "ODO"
5. Click "ODO % sat"
6. Review the temperature value on the screen and make sure it is stable.
7. Using the BBP's calibrated YSI ProPlus handheld meter, enter the current barometric pressure value in mmHG.
8. Choose 1 point calibration and make sure the calibration standard shows up properly as air saturated (this can be set by clicking the Gears icon, Calibration submenu icon, ODO icon, ODO % sat icon, and then selecting "air saturated" followed by clicking apply).
9. Click "Start Cal"
10. Once the temperature value has stabilized and "unstable data" in red font changes to "stable data" in green font, click "apply".
11. Verify the "Pending (Post) value is correct and click "Complete".
12. The calibration worksheet for the probe will pop up and the user should record the following three values:
 - a. Pre Calibration Value: record this value in the data sheet's "Before Cal" column.
 - b. Post Calibration Value: record this value in the data sheet's "Calibrated" column.
 - c. DO Gain: record in the data sheet's "Sensor Diagnostics/Pre-Deployment" optical DO gain field.
13. Review the DO Gain to make sure it is within the recommended 0.87 – 1.25 range
14. Print the calibration worksheet.
15. Close the calibration worksheet.

YSI Tips:

DO probe sensor caps should last 1–2 years (possibly longer), but do require replacement once its lifespan has ended. For optimum performance, Optical DO sensor membranes must be kept fully hydrated in water. If your DO probe has been dry-stored, it will need to hydrate in saturated tap water over night. If the probe was stored in saturated air the sensor should be placed in saturated water for a few hours to ensure full hydration. Always make sure that the DO membrane is clean and free of any slime or mold.

4.0 PROGRAMMING & DEPLOYMENT PREPARATION

4.1 Programming:

1. Click Gear icon, Click "Update Time"
 - a. Make sure your PC is set to standard time.
 - b. Click box next to "Relative to PC".
 - c. Click "Apply"
2. Click Large Green Arrow icon.
 - a. Click "Read Current Sonde Settings" submenu icon.
 - b. Click Screwdriver & Wrench icon.
 - c. Enter a template file name (each station has a template) and choose deployment Time Zone.
 - d. The user will also see three clickable tabs:
 - i. Basic
 1. Logging Interval (Hour:Minute:Second): enter as 0:15:0
 2. Username: enter as user wishes.
 3. Site Name: choose from drop-down menu list of station names entered into KORS using the Map icon (See KORS software section).
 4. File name prefix: characters entered here will be the first ones used in filenames.
 - ii. SDI-12: used in telemetry applications
 - iii. Advanced: used to enable sample and hold for sondes placed at telemetry sites along with other advanced logging options.
 - e. Click "Apply"
3. Once the information has been set in the above three tabs, click the small green arrow icon (says Save, Deploy, Start Logging when moused over).
4. Choose a start time (either setting a time when the instrument will be deployed or if on site, using "Next Interval" and click "apply").
5. The "Current Deployment Summary" screen will show up containing a number of values needed for filling out the "Programming" section of the data sheet. Record the following from this summary page on the data sheet:
 - a. Start Date
 - b. Start Time (standard time)
 - c. Sonde Filename: name of the .BIN file
 - d. Battery Life (days): labeled as "Battery Life Remaining" in EXO (NOTE: This value may be inaccurate during cabled communication as the PC is providing power to the EXO. Checking battery life via a Bluetooth connection yields a more accurate number of days).
 - e. Free Memory (days): labeled as "Logging Space Duration
 - f. Free Memory Status (bytes or %): labeled as Log Space Available in % in EXO

6. The sonde is now ready for deployment!

4.2 EXO Deployment

The sonde is now ready to be deployed at their station.

1. Make sure each sonde has a white label taped to the sonde body indicating the sonde nickname, serial number, date of deployment and station ID.
2. When transporting the sondes, a tap-water-soaked white towel must be wrapped around each sonde. This is to be done during both deployment and upon retrieval. The wet towels reduce shock and vibration damage and ensure a saturated environment for the oxygen probe during transport. This task is *MANDATORY* to improve the oxygen data we are collecting.
3. Sondes should be transported in a cooler of sufficient size to allow them to lie horizontal across the bottom. Suggested size is 28" x 15" x 14" for up to 4 sondes.
4. All sondes are to be deployed so that the probes stay submerged at low tides and are at a fixed distance off the bottom to allow for tidal and flow amplitude measurements. Suggested methods include a perforated PVC (or other plastic) tube attached to a pile of bridge abutment or a steel cage resting on the bottom (be sure probes are 0.25 to 0.5 meter off bottom). If you use a perforated tube, this tube must be periodically inspected for fouling and cleaned.
5. The length of time the instrument is deployed is dependent on the rate of fouling at your site. This will range from less than a week to up to a maximum of four weeks.
6. Independent, paired field data readings are required at all sonde retrievals/deployments. Use a YSI ProPlus hand-held meter or other properly calibrated instrument to collect this data alongside the deployed sonde for its last reading and the newly deployed sonde for its first reading. At a minimum, you must take an independent paired reading with the freshly calibrated sonde against the deployed sonde before replacing. Record the data from the independent instrument in the Deployment and Retrieval Information and Field Log sections on the BBP Continuous Water Quality Monitoring Program Calibration Log.
7. PVC deployment tubes:
 - a. Service the tubes annually
 - b. To check on the integrity of the installation tube, deploy a second sonde outside the tube and at the same depth. Compare the data from the two sondes. If the tube is fouled, the sonde inside will only be recording the microcosm of the pipe, not the water itself.

5.0 EXO RETRIEVAL

1. Retrieve the sonde from the water and visually examine it and the probes for fouling and/or damage. Note any fouling type and amount in the "Fouling Presence" section of the Water Quality Field Log, however DO NOT remove fouling, so that true post-

deployment readings may be obtained. Obtain photos of the sonde body and probes/bulkhead to be stored on the shared drive.

2. Record field data with a ProPlus for the following mandatory parameters on the data sheets: water temperature, specific conductivity, salinity, pH, pH millivolts, barometric pressure, DO percent saturation, DO concentration and instrument used to take measurements. Additional optional parameters may be recorded in the "Other" field of the data sheet.
3. Wrap the EXO sonde in a tap-water saturated white towel and placed in a secure container in order to prevent severe vibrations to the EXO sonde during transportation.

6.0 EXO DATA DOWNLOAD & POST-DEPLOYMENT READINGS

NOTE – Post deployment readings and checks note any changes or drift of the probe during deployment combined with effects of biofouling. This process is critical not only for data QA/QC, but also for data users to know if the data were affected by biofouling, wear and tear, or other issues. Ideally these checks will take place within 24 hours of EXO sonde retrieval. If not, it is critical to make a visual inspection of the conductivity cells and note, either photographically or via notes, any visible fouling to document related drift. Bubbles and saturated water bath currents may dislodge material and significantly impact drift.

6.1 Data Download

1. Place the EXO sonde into a bucket of clean water that has been aerated for at least 60 minutes to create a 100% air saturated water bath. Allow the sonde ample time to reach temperature equilibration prior to beginning the download and post-deployment readings procedures.
2. Connect to the EXO sonde via the USB/SOA adapter or wirelessly via Bluetooth.
3. Click Large Green Arrow icon
4. Click Stop Logging
5. Click Data Folder icon
6. Click "Transfer"
7. Click to highlight the file of interest
8. Click "Selected"
9. Click "View/Export"
10. If a PC folder window comes up, click the file of interest in that window and click "okay". If it does not pop up, click the small blue folder icon that says "select file" when you mouse over it (NOT the Main Data folder icon), select the file and click "okay".
11. Click the icon next to the small blue folder icon (two white pages stacked on each other) that says "export data" when moused over.

12. Two files should now be visible in the "Data Files" folder within the KORS folder on the PC hard drive; a .BIN file and an Excel file, the latter of which often opens automatically
13. Do NOT remove the sonde from the aerated water bath yet.

6.2 Post-Deployment Readings

These readings are taken in discrete mode via the Green Running Man icon and exhibit many procedural similarities to the calibration procedure. While not specifically listed by step by step, the same rinsing procedures between readings for each probe as detailed in the Calibration Section should be followed. Values recorded during Post-Deployment checks are written in the "Post-Deployment" or "Sensor Diagnostics" sections of the WQ Data Sheet.

1. Place the YSI ProPlus into the aerated bucket with the sonde. Reconnect to the sonde if necessary.
2. Click the Green Running Man icon.
3. Record the temperature reading given by the EXO sonde and YSI ProPlus handheld, remembering to record the corrected temperature for both instruments.
4. Record the DO % saturation readings taken in the air saturated water bath in the post-deployment section of the data sheet.
5. Remove the EXO from the saturated water bath
6. Remove the guard and using an Allen wrench, remove the wiper from the wiper brush from the central wiper assembly. Clean all debris from the brush immediately. Soak the brush in water with mild detergent. Remove brush, rinse well and use a small o-ring to keep bristles from drying with gaps. Place the freshly cleaned wiper to the side to dry as it is no longer needed for this section.
7. Place sonde in a water-saturated air environment (loosely fitted calibration cup with a tiny amount of water in it). While in discrete mode, record the water depth/level value given by the EXO sonde and the barometric pressure reading from the handheld.
8. Record post-deployment pH readings and diagnostic millivolt readings on the data sheet by running the EXO sonde in discrete mode in each of the 3 pH standards. Careful to rinse in between each calibration check.
9. Disconnect the sonde from KORS (remove the adapter for cabled communication or put the EXO sonde to sleep with the magnet tool for blue tooth connection).
10. Clean the EXO sonde thoroughly. All fouling should be removed at this point to avoid contamination of the turbidity standards.
11. Reconnect the sonde to KORS
12. Take discrete readings in both distilled water and 126 FNU standards (remember that the EXO interprets the 126 FNU YSI standard as 124 NTU) and record those values in the Post-Deployment section of the data sheet.
13. Record the battery voltage

14. The EXO may now be removed from the water bath and prepared for storage until its next deployment.

7.0 PROBE CARE & STORAGE

Most of the probes, except Conductivity, have a limited shelf life so do not purchase replacements too far in advance. The procedure for storage of probes is different for short-term (1 month or less) and long-term (greater than 1 month). Please refer to the EXO user manual for more detailed instructions and recommendations regarding storage and care.

7.1 Short-term Storage

For short term storage, it is important to keep the probes moist but not immersed in water. Keep probes attached to the EXO sonde and place the sonde in approx. 0.5 inches of tap water (not distilled) in the sealed EXO calibration cup.

7.2 Long-term Storage

1. Probes/sensors: All probes should be cleaned and dried thoroughly and then stored in their original box with caps on where appropriate. Each probe was shipped with a cap to cover the connector; these should also be placed on the probes for long term storage.
 - a. Clean conductivity sensors and store them dry.
 - b. The pH probe should be stored in the pH storage cup (the one it was shipped in) containing 1 molar KCL or pH 4 buffer.
 - c. No special precautions are necessary for the Depth sensor.
 - d. Store the turbidity probe dry in air and cover the optical surface with a cap to prevent scratching
 - e. Dissolved Oxygen probes should be stored in the cap it was shipped in. This cap has a small sponge that should be kept moist to maintain a water-saturated air environment to avoid the need for a 12 hour membrane rehydration at a later date. This sponge should be checked periodically to make sure it remains moist. The probe can be stored dry, but if done so it must be re-hydrated in saturated water for a 12 hour period.
 - f. Remove the brush from the wiper probe and store dry (make sure it is clean and dries in original shape – no gaps or forks in the bristles). The wiper itself can be stored in its original box with cap over connector.
 - g. Remove copper tape applied directly to the sensors prior to long-term storage to prevent the glue from hardening and becoming difficult to remove. Copper tape can remain in place if a protective barrier is applied underneath like packing tape or YSI clear anti-fouling sleeves.

2. For EXO sondes:

- a. Remove batteries prior to storage greater than 30 days.
- b. The battery compartment and compartment cap should be cleaned thoroughly and re-greased prior to storage.
- c. Clean and re-grease the two sonde connectors (located at the top of the sonde) and place connector caps on both
- d. Plug ports of any missing sensors.

8.0 TURBIDITY STANDARD DILUTION

Turbidity standard dilutions will be performed in the OCC Biology prep lab located in the Heiring Science Building, room 122. The prep lab is open and available to BBP staff on Mondays between 8am and 4pm. Barbara Collins must be notified via email or phone prior to coming to the lab.

Email: bcollins@occ.edu

Phone: ext. 2293

Supplies:

10 ml pipette – in biology prep lab
500 ml glass Erlenmeyer flask - in biology prep lab
500 ml graduated cylinders - in biology prep lab
Distilled Water
4000 ntu formazin standards

Procedure:

This procedure will make 400ml of 100 NTU formazin standard. This is a 1 time use calibration standard.

1. Invert the 500ml bottle of 4000ntu stock formazin standard 10 times or until all settled solids have mixed into solution. Vigorous mixing is not recommended, however some mixing is necessary.
2. Using a pipette or bulb; pipette 10 ml of 4000ntu formazin stock solution into a clean, dry 500ml Erlenmeyer flask or 500ml graduated cylinder.
3. Slowly add distilled water to the flask until the meniscus reaches the 400ml gradation using the rinse bottle to carefully add distilled water. Do not over fill.
4. Seal the opening with a stopper or parafilm and mix gently by inverting. DO NOT shake vigorously as this will create air bubbles which will trap light and produce inaccurate measurements.
5. Clean the pipette carefully and thoroughly then set to dry.

Other dilutions can be made using the following formula:

$$C_1V_1 = C_2V_2$$

Where: V_2 = Final volume of new solution. C_2 = Final concentration of new solution.

Ex. $(4000 \text{ NTU}) \times (V_1) = (100 \text{ NTU}) \times (400 \text{ ml})$

$$V_1 = (100 \text{ NTU}) \times (400 \text{ ml}) / 4000 \text{ NTU}$$

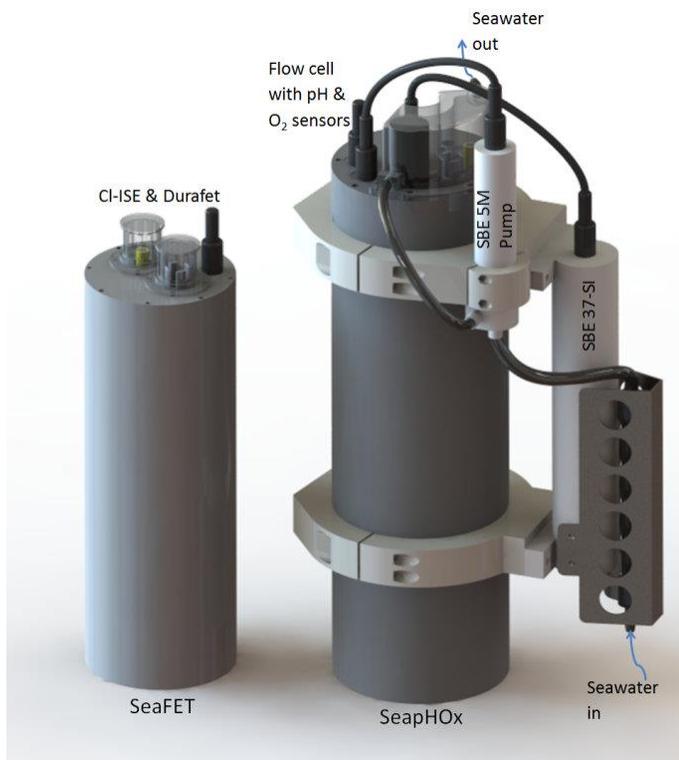
$$V_1 = 40000 \text{ ml} / 4000$$

$$V_1 = 10 \text{ ml}$$

Storage:

Place used calibration standard in a labeled container to be used as a rinse standard for the next calibration. Discard used rinse standard per the manufacturers' recommendations.

California Current Acidification Network (C-CAN)



**Best Practices for
autonomous
measurement of
seawater pH with
the Honeywell
Durafet pH sensor**

Todd Martz, Karen McLaughlin, Stephen B. Weisberg

March 2015

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Preface

The California Current Acidification Network (C-CAN) is a collaboration dedicated to advancing understanding of ocean acidification (OA) and its effects on biological resources of the U.S. West Coast. C-CAN first convened in 2010 in response to a growing realization that declines in shellfish hatchery production corresponded to coastal upwelling of low pH waters. The initial workshop brought together leading shellfish industry representatives, coastal managers, researchers, Sea Grant programs, and Integrated Ocean Observing Systems to increase collective understanding of OA effects on the nearshore environment. C-CAN has since expanded to include other ocean-dependent industries, environmental advocacy groups, regulatory agencies, and tribal groups.

The overarching goal of C-CAN is to coordinate and standardize OA measurement and data collection practices, ensuring data accessibility, utility, and application. C-CAN provides shared guidelines and support for participating groups in implementation of high quality, compatible monitoring programs. C-CAN also facilitates application of the network's data in developing tools that examine the causes of ecosystem impacts and predict future changes in ocean chemistry and biological communities. Finally, C-CAN communicates its findings to address management concerns about defining the ecological effects of OA for development of mitigation and adaptation strategies. Given the complexity of this emerging issue, and recognizing that advancing knowledge will require a concerted community effort, C-CAN is committed to serve as the region's source of reliable, vetted scientific information on ocean acidification.

Introduction

Coastal ecosystems are vulnerable to ecological and biogeochemical perturbations from ocean acidification (OA) (Doney et al. 2009, Howarth et al. 2011). However, determining the effects of OA on nearshore ecosystems, including coastal and estuarine waters, is difficult due to the interplay of numerous factors including freshwater inputs, tidal forcing, water stratification, nutrient over-enrichment, algal blooms, and hypoxia (Fabry et al. 2008, Borges and Gypens 2010). Understanding the impacts of OA in the coastal environment requires coordination of monitoring efforts to ensure that intercomparable data on OA and its effects on nearshore ecosystems are collected. The California Current Acidification Network (C-CAN) was initiated, in part, to address these issues. C-CAN has developed a vision that lowers barriers to making seawater CO₂ measurements of sufficient quality to understand ecosystem effects of changing ocean chemistry¹. One of C-CAN's core monitoring principles is that seawater OA measurements should facilitate determination of aragonite saturation state (Ω) and a complete description of the carbonate system (McLaughlin et al. 2014). This requires direct measurement of at least two carbonate system parameters, of which seawater pH is considered a master variable for understanding the impacts of OA on coastal ecosystems.

Ion Sensitive Field Effect Transistor (ISFET) pH sensors have been found to be stable and accurate for monitoring fine-scale changes in pH in open ocean environments (Le Bris and Birot 1997, Martz et al. 2010) and are becoming widely-accepted for open ocean and nearshore monitoring of high frequency variability in pH (Hofmann et al. 2011, Kroeker et al. 2011, Yu et al. 2011). However, to date there have been no broadly agreed upon best practices for deployment of such sensors. C-CAN's efforts to develop a coordinated monitoring program documenting changing ocean chemistry have led to a growing number of non-specialist users who are adopting ISFET sensors for continuous, autonomous measurement of pH in a variety of settings, exposing a need for coordinated best practices for deployment of ISFET sensors and data quality assurance and quality control. Clearly defined best practices for deployment of ISFET sensors is critical for assessing data quality and intercomparability across users, which is crucial to interpreting data from a network of sites.

The purpose of this document is to provide broadly applicable recommended protocols for autonomous pH sensors incorporating the Honeywell Durafet (based on the published work of Bresnahan et al., 2014). The Honeywell Durafet pH sensor is a commercially available and widely used sensor, which has been deployed in a variety of configurations by different users. The recommendations in this document evolved from sensor deployments carried out in various locations since 2009.

Recommendations are summarized below and a brief discussion of each point is provided on the following pages. Recognizing that not all recommendations can be practically met, the primary recommendation for all sensor users is embodied in the final protocol regarding error reporting.

¹ More information on C-CAN's vision can be found in a companion document available at: <http://c-can.msi.ucsb.edu/c-can-documents/C-CAN%20%20Vision%20Document%20Final.pdf/view>

Recommended Protocols

1. Preceding deployment, operate sensors in natural seawater until initial sensor drift due to conditioning ends (approx. 5-10 days), with daily samples in order to observe the pre-deployment conditioning period; repeat this process following deployment for validation. Power the ISFET continuously during this period.
2. Collect a careful shore-side calibration point based on discrete sample(s) following the conditioning period.
3. Store sensors in seawater between deployments.
4. Prevent biofouling as permitted, especially within the euphotic zone.
 - i. Utilize an actively flushed flow scheme that minimizes light.
 - ii. Incorporate a Sea-Bird instrument with tributyltin plugs into the flow scheme.
 - iii. Wrap sensor housings with tape (McMaster-Carr P/N 6029T98) and paint with EP-SN1 or similar antifouling paint.
 - iv. When using passively flushed SeaFET sensors, incorporate a 70:30 Cu-Ni alloy tube into a flow stream around Durafet and ISE.
5. When practical, take frequent discrete samples alongside a sensor throughout a deployment in order to establish an error estimate in the sensor data. At minimum collect one bottle sample alongside an operating deployed sensor.
6. Deploy co-located, independent sensors such as redundant pH, $p\text{CO}_2$, and O_2 sensors.
7. Estimate pH from regional empirical and/or thermodynamic relationships.
8. Assess and control pH sensor data quality with discrete pH and estimated pH using the following plots:
 - i. *time-series anomaly* to first identify and then eliminate periods of ostensible sensor conditioning, drift, and failure.
 - ii. *property-property* to examine agreement between sensor pH and an independent reference pH (through the intercept, c_0 , & slope, c_1). Property-property plots are useful for quality assessment; that is, a c_0 significantly different from 0 and/or c_1 from 1 indicates bias in the sensor and/or reference pH used for comparison.
9. Apply a single calibration point, chosen to minimize the anomaly relative to a trustworthy reference pH throughout the deployment. In particular, it is not recommended to force sensor data to agree with multiple individual bottle samples as this imparts sampling error to the sensor time series.
10. Establish an error envelope for the sensor time-series. The accuracy of the sensor time-series can be no better than the reference to which it is calibrated or validated.

About the sensors

Ion Sensitive Field Effect Transistor (ISFET) pH sensors can be deployed in a variety of configurations. This set of guidelines is based on experience with the “SeaFET” design (commercialized by Satlantic, L.P.), which consists of a Honeywell Durafet and a solid-state chloride ion selective electrode (Cl-ISE) (Martz et al., 2010), though many of these recommendations apply broadly to other ISFET and glass electrode pH sensors.

Unlike potentiometric glass electrodes, the ISFET sensor is an active electronic device, based on Metal Oxide Semiconductor Field Effect Transistor (MOSFET) technology. When exposed to solution, the oxide

coating of the MOSFET's conduction channel exchanges protons (hydrogen ions), giving rise to an interface potential that is measured as a voltage between the source of the MOSFET and a reference electrode. For further details the reader is referred to Bergveld (2003). In the SeaFET, the ISFET voltage is recorded relative to two independent reference electrodes: an internal Ag/AgCl reference with a liquid junction and a junctionless external Cl-ISE, referred to hereafter as E_{INT} and E_{EXT} , respectively (Martz et al., 2010).

The pH of seawater is calculated from the measured sensor voltage using the Nernst equation to relate sensor voltage to hydrogen ion concentration. Corresponding pH values for the internal and external reference electrodes, pH^{INT} and pH^{EXT} , are derived from the internal and external voltages respectively, the temperature of the solution, and a calibration constant (termed "E0" in Note 2 below, E^* in Bresnahan et al., (2014), and sometimes referred to as K_0 , or E^0). A single-point calibration, specific to each reference electrode, defines the intercept (E0) in a line of pH vs. sensor voltage at the in situ calibration conditions. Thus, the calibration point is specified as a sensor voltage at a particular pH, temperature, and salinity. Sensor voltages are extended over a range of pH, temperature, and salinity by assuming a 100% Nernst slope and that the relative change in voltage with temperature is constant. The reader is referred to Note 2 and Bresnahan et al. (2014) for equations and further details.

The dual reference electrode design is not a requirement, but can aid in evaluating data quality. Due to the difficulty of achieving a stable potentiometric reference (Culberson, 1981), the two independent reference electrode design provides a theoretical improvement due to the fact that the liquid junction potential of the internal reference is unquantifiable and therefore adds uncertainty to the pH_{INT} value, an uncertainty that can be evaluated with the external reference (Martz et al., 2010). However, experience has also shown that the internal reference electrode is of the highest quality and, under many circumstances, appears to remain nearly as stable as the external reference. Consequently, retaining two reference electrodes provides a simple check during data QC: differences between pH_{INT} and pH_{EXT} serve as an indicator of sensor malfunction and/or fouling. However, users should be cautioned, due to the unmeasurable liquid junction potential, pH_{INT} has a poorly characterized (yet small) salinity response that leads to increasing errors as salinity departs from that at the time of calibration. Although this error in pH_{INT} is presumed to be small over narrow salinity ranges, this may not be the case if there are large salinity variations. The thermodynamic uncertainty due to the liquid junction potential cannot be ignored when the sensor is deployed in coastal locations with significant freshwater input or large temperature variability. However, in test tank experiments over the salinity range 30-36, an effect on the liquid junction potential could not be identified and therefore a salinity correction for the pH_{INT} under typical seawater conditions is not recommended (Bresnahan et al., 2014).

Discussion of Recommended Protocols

Recommendation 1. Preceding deployment, operate sensors in natural seawater until initial sensor drift from sensor conditioning ends (approx. 5-10 days).

When first placed in seawater, pH sensor voltages relative to both reference electrodes exhibit an asymptotic drift (Figure 1). This conditioning period is due to several factors: 1) the time required to achieve a stable flow of ions across the liquid junction of the internal reference electrode (nominally hours), 2) the time required to replace chloride ions with bromide ions in the solid solution of AgCl in the

CI-ISE (nominally days), 3) the time required for an ISFET conditioning component, related to the initial power-up of the chip, the exact basis of which is not fully understood (nominally 1 day), and 4) a pressure effect on the ISFET and internal reference electrode through changes in the liquid junction potential that may become important if the sensor is deployed more than ~20 m below the surface (nominally 1 hour). Factors 1-3 can be addressed by operating the pH sensor continuously in seawater (never powering off the ISFET) for one week prior to deployment and taking care to keep the sensor wetted in natural seawater during transport. If these preconditioning procedures are ignored, the sensor may exhibit drift during the first days of a deployment. The fourth aspect of conditioning (a pressure effect) is problematic to characterize as it appears to be sensor specific and not necessarily repeatable. Using the Durafet sensor for profiling applications in the 0-80 m range (rated depth) is therefore discouraged. However, Durafets have been successfully operated at 80 m for extended periods; the key to a successful deployment rests in selecting an appropriate reference pH once the sensor is deployed and conditioned at depth.

As a result of these experiments, best practices should include pre-deployment operation of Durafet sensors in natural seawater until the initial sensor drift due to conditioning is finished (approx. 5-10 days). Furthermore, daily samples of discrete pH should be collected in order to observe the pre-deployment conditioning period; a process which should be repeated following deployment for validation. The ISFET should be powered continuously during this period and throughout the deployment.

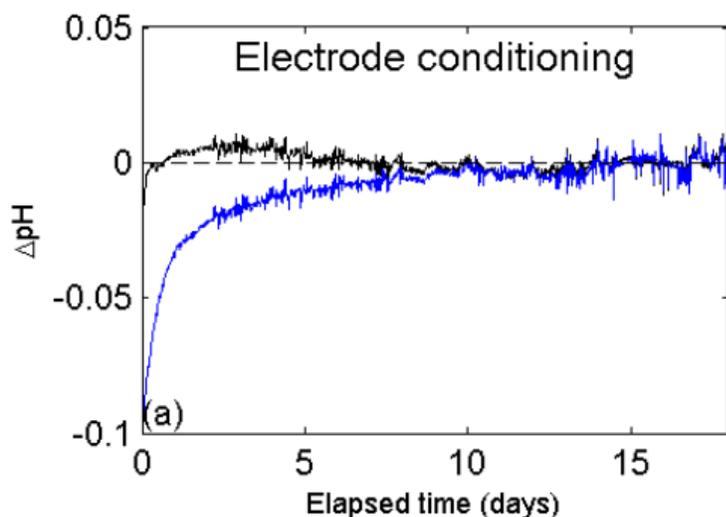


Figure 1 (From Breshahan et al, 2014, Figure 5a). Time series anomaly of difference between pH measured by internal reference electrode pH^{INT} (black) and external reference electrode pH^{EXT} (blue) compared to continuous measurements of pH measured by a continuous underway spectrophotometric pH system. Black dashed lines represent a zero anomaly. Asymptotic drift at the start of each deployment to zero anomaly represents the conditioning period for each reference electrode.

Recommendation 2. Best practices require a careful shore-side calibration point based on discrete sample(s) following the conditioning period.

Whether or not sensors are factory-calibrated, we recommend checking the calibration or establishing a new calibration point on shore before deployment. The initial accuracy of a stable sensor is limited by the calibration approach. Trust in pre- and postcalibrations (i.e., setting calibration constants before sensors are deployed or after they are recovered) of any marine chemical sensor relies on two hard to satisfy criteria: 1) sensors must be calibrated in a similar physical setting (i.e., similar temperature,

salinity, pressure) to that of the study location and 2) sensors must not undergo significant (re)conditioning in their new environments (See Recommendation 1). It is always preferred to rigorously calibrate a sensor before deployment, but this may require facilities and time that are not available. Honeywell provides an initial factory calibration of every Durafet sensor on the NBS pH scale, but provides no statement of calibration accuracy or stability, recommending that the user perform the canonical NBS buffer standardization employed widely for all glass electrodes. Because the NBS pH scale is not recommended for seawater pH measurements (Marion et al., 2011), at minimum, the Honeywell Durafet must be recalibrated on the appropriate pH scale (C-CAN recommends use of the total hydrogen ion scale, see Note #1) before use in oceanographic applications. Due to these complications, it is recommended that the user calibrate an operating Durafet to a discrete measurement of pH taken shore-side after the sensor is conditioned. This practice also serves to validate laboratory calibration. The calibration sample must coincide in time and space with the comparison sensor measurement.

Matlab code is provided at the conclusion of this document (Note 2) to enable a user to derive calibration coefficients for the internal and external reference electrodes (**pHCalib.m**) and utilize those calibration coefficients to calculate pH from the measured time-series voltages on each electrode during deployment (**pHCalc.m**).

Recommendation 3. Store sensors in seawater between deployments.

Following initial conditioning period (Recommendation 1), sensors should be transported to the deployment site and maintained in natural seawater between deployments to minimize potential reconditioning, and associated sensor drift, in a new environment. Although placing a sensor in a low ionic strength solution such as freshwater or standard buffers will not damage the sensor, the sensor may condition to these solutions if placed in them, requiring reconditioning once placed in a saline environment. The sensor should be also be powered continuously during the time following conditioning in order to avoid the warm-up period associated with powering ON the ISFET sensor.

Recommendation 4. Prevent biofouling as permitted, especially within the euphotic zone.

Biofouling is the leading cause of measurement error in the nearshore environment, dominating the time series anomaly signal on the weekly to monthly timescales (Figure 2). Thus prevention of biofouling is critical in these environments. The approach to biofouling prevention has been evolving as experience with the in situ Durafet sensor grows and is expected to continue to improve. Presently, to minimize biofouling, it is recommended that users utilize an actively flushed flow scheme that minimizes light, such as that incorporated into the SeapHOx configuration. Actively flushed (i.e., pumped) sensor packages show far greater stability than passively flushed packages, with the former remaining stable in a wide variety of environments on timescales approaching one year, and the latter often succumbing to biofouling within one month. Below the euphotic zone, the flushing scheme appears to be less important, with both packages remaining stable for greater than nine months. In addition, incorporation of a Sea-Bird instrument with tributyltin biocide plugs into the flow scheme is also recommended. Sensor housings should be wrapped with tape (McMaster-Carr P/N 6029T98) and painted with EP-SN1 or similar antifouling paint. The enclosures block most light, which not only reduces biofouling, but also mitigates the direct impact of light on sensor response, which can be substantial for an ISFET. If the user is deploying a passively flushed SeaFET sensor, it is recommended that they incorporate a 70:30 Cu-Ni

alloy tube into a flow stream around the Durafet and ISE, which has proven superior to the original Cu mesh.

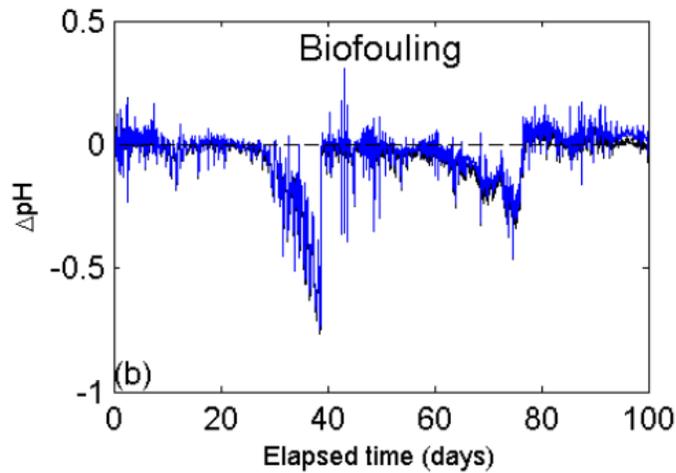


Figure 2 (From Breshahan et al, 2014, Figure 5b). Time series anomaly of difference between pH measured by the internal reference electrode pH^{INT} (black) and external reference electrode pH^{EXT} (blue) compared to continuous independent measurements of pH from the internal pH reference electrode of a stable co-deployed SeapHOx sensor package on a mooring. Black dashed lines represent a zero anomaly.

Recommendation 5. When practical, take frequent discrete samples alongside a sensor throughout a deployment in order to establish an error estimate in the sensor data.

Several factors that affect the ideal bottle sampling frequency include length of deployment, access to study site, rate of fouling, availability of co-located sensors, and access to real-time data. For example, it may be helpful to collect weekly bottle samples for an easily accessed sensor in a high fouling environment, while open ocean locations may be limited to bottle measurements at the time of deployment and recovery.

As noted above, pH sensor measurements are ideally calibrated with a single E0 that minimizes the difference between trustworthy, discrete pH measurements, assessed using standard bench top procedures (Dickson et al., 2007) and the sensor measurements. Frequent, discrete measurements should be collected to both establish an error estimate for the sensor time series, as well as to identify when the sensor data become suspect due to fouling, sensor drift or battery failure. Discrete measures of pH serve as an independent sensor validation point(s) following initial calibration and care should be taken when using discrete measurements to apply corrections to sensor data during post-processing (see recommendation 9).

Recommendation 6. Deploy co-located, independent sensors such as redundant pH, pCO_2 , and O_2 sensors.

Although not a requirement, co-located sensors can augment a time-series in ways that bottle samples cannot. Sensor redundancy provides a powerful cross check for discerning data quality. Comparison of two independent measures of pH, or a variable that is expected to co-vary with pH such as dissolved oxygen or pCO_2 , can help to identify sensor problems such as the onset of fouling. Without independent validation based on bottle samples (per Recommendation 5), additional sensors, or post-calibration, the output of any sensor must be skeptically viewed. Simply put, in a situation where a single pH electrode

(ISFET, glass, etc.) is deployed with a single reference electrode in the absence of additional biogeochemical sensors or discrete samples to provide data quality control, the resulting pH time-series should be viewed as unsubstantiated. We acknowledge that these requirements add complexity to sensor deployments but suggest that the returns in data quality are worth the effort. The Durafet sensor packages offer resolution that can't practically be matched by discrete sampling programs and have gained popularity due to their ease of use and low cost. Investment in a redundant pH sensor, or co-location with a dissolved oxygen or pCO₂ sensor will insure data quality, and in the case of oxygen and pCO₂ sensors will provide additional biogeochemical contextual data for analysis.

Recommendation 7. Estimate pH from regional empirical and/or thermodynamic relationships.

Co-located chemical sensors can be used to derive empirical pH values which can then be used in lieu of measured pH data to evaluate sensor performance and characterize sensor malfunction and/or drift. These relationships are regional in nature and must therefore be calibrated to each new area and re-evaluated over time. For example, Alin et al. (2012) report several empirical relationships between pH, pCO₂, O₂, temperature, and salinity. In combination with relationships such as these, thermodynamic equations from the program CO2SYS for Matlab (van Heuven et al., 2011) can be used to derive an estimated pH. Most commonly, regional relationships for estimating total alkalinity as a function of temperature and salinity, TA^{est}, are combined with co-located pCO₂ sensor data to estimate pH from pCO₂ and total alkalinity. Combining the error in TA^{est} (6.4 μmol·kg⁻¹ as defined by Alin et al. 2012) and pCO₂ (less than 5 μatm), the propagated error in the estimated pH would be less than 0.01 pH units using CO2SYS (Bresnahan et al. 2014).

Figure 3 demonstrates how use of a co-located dissolved oxygen sensor and the regional algorithm for estimating pH from Alin et al. 2012 was used to identify drift in the internal reference electrode. The internal and external reference electrodes began to deviate from one another after 100 days of deployment, use of the oxygen sensor to estimate pH enabled identification of the external reference electrode as providing accurate pH data. Without the oxygen data, it would have been impossible to pinpoint the source of pH sensor drift between the ISFET, internal reference, and external reference electrode. The drift in pH^{INT} relative to pH^{EXT} would have signaled a problem with the system and both pH values would have been flagged as 'bad.'

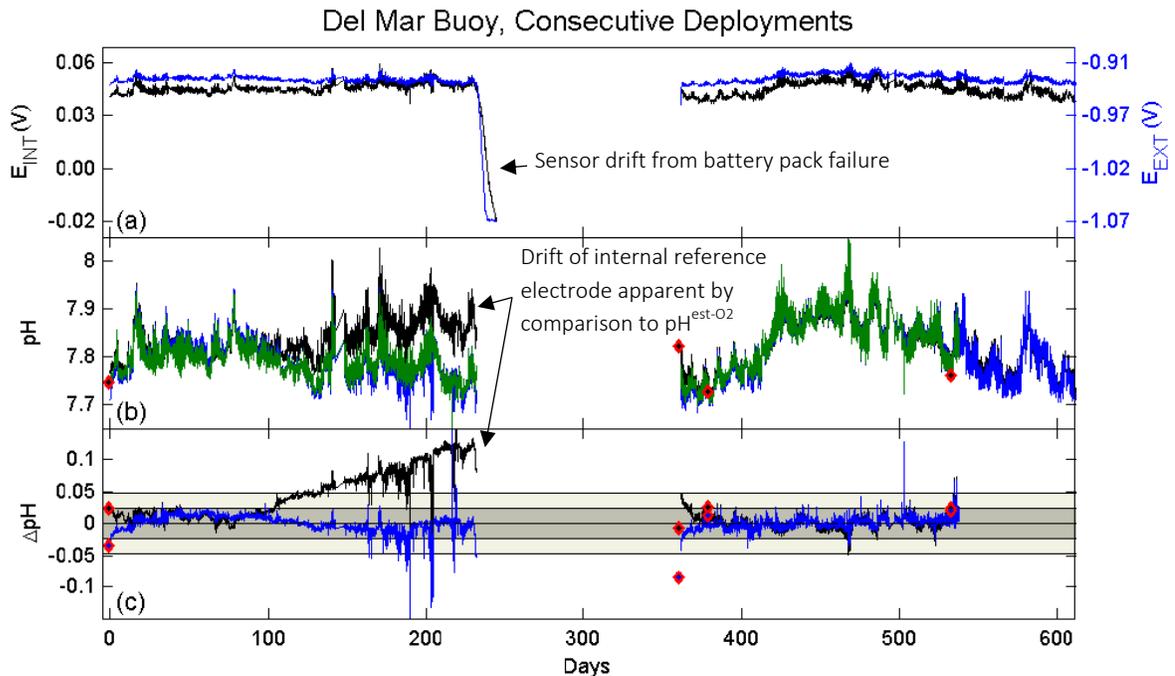


Figure 3 (From Breshahan et al, 2014, Figure 2). Del Mar Buoy pH time-series beginning on 25-Jun-2011. (a) Raw sensor voltages for internal (black) and external (blue) reference electrodes show two consecutive deployments with a four-month gap. (b) pH is calculated using the internal (pH^{INT} , black) and external (pH^{EXT} , blue) reference electrodes and estimated from oxygen and temperature ($\text{pH}^{\text{est-O}_2}$, green). Discrete sample values are black diamonds with red edges. (c) Anomalies (ΔpH) for pH^{INT} (black) and pH^{EXT} (blue) are shown relative to $\text{pH}^{\text{est-O}_2}$ (solid lines) and discrete samples (filled diamonds, red edges) with σ (dark gray) and 2σ (light gray) shaded regions, where standard error in $\text{pH}^{\text{est-O}_2}$ as reported by Alin et al. (2012) is 0.024 pH units. The optode failed on 15-Dec-2012 but the SeaFET functioned until 28-Feb-2013, leaving the pH time-series without a $\text{pH}^{\text{est-O}_2}$ value for the last 75 days.

Recommendation 8. Assess and control pH sensor data quality with discrete pH and estimated pH using the time-series anomaly and property-property plots.

Time-series anomaly plots, wherein the time-series of the differences between sensor pH and an independent assessment of pH are shown, can be used to first identify and then eliminate periods of ostensible sensor conditioning, drift, and failure. pH anomalies are reported as ΔpH^{i-j} where i and j refer to two independent measures (or empirical estimate(s)) of pH. Time-series anomaly plots act as a screening tool for acceptable data.

Similarly, property-property plots can be used to examine agreement between sensor pH and an independent, reference pH. Sensor offset (i.e., intercept, c_0), and slope (c_1), relative to an independent, reference pH value (pH estimated from discrete samples, pH estimated from O_2 , or pH estimated from pCO_2) can be calculated from a Model II least squares fit (Peltzer, 2007) of property-property plots (namely, $\text{pH}_{\text{sensor}}$ vs. $\text{pH}_{\text{reference}}$). Property-property plots are useful for quality assessment; that is, a c_0 significantly different from 0 and/or c_1 significantly different from 1 indicates bias in the sensor and/or

reference pH used for comparison. Examples of property-property plots are given below in Figure 4. Note that when computing a c_0 , to assess the presence of sensor offset, it may be preferable to scale the regression equation to the observed range of pH values such that the lowest values measured correspond to the graphical origin (i.e., in Figure 4a, $y = c_0 + c_1x$ becomes $y = 8.1 + c_0' + (x - 8.1)c_1$). Thus, the c_0' value and its associated error better reflect sensor performance over the range of values observed by the instrument.

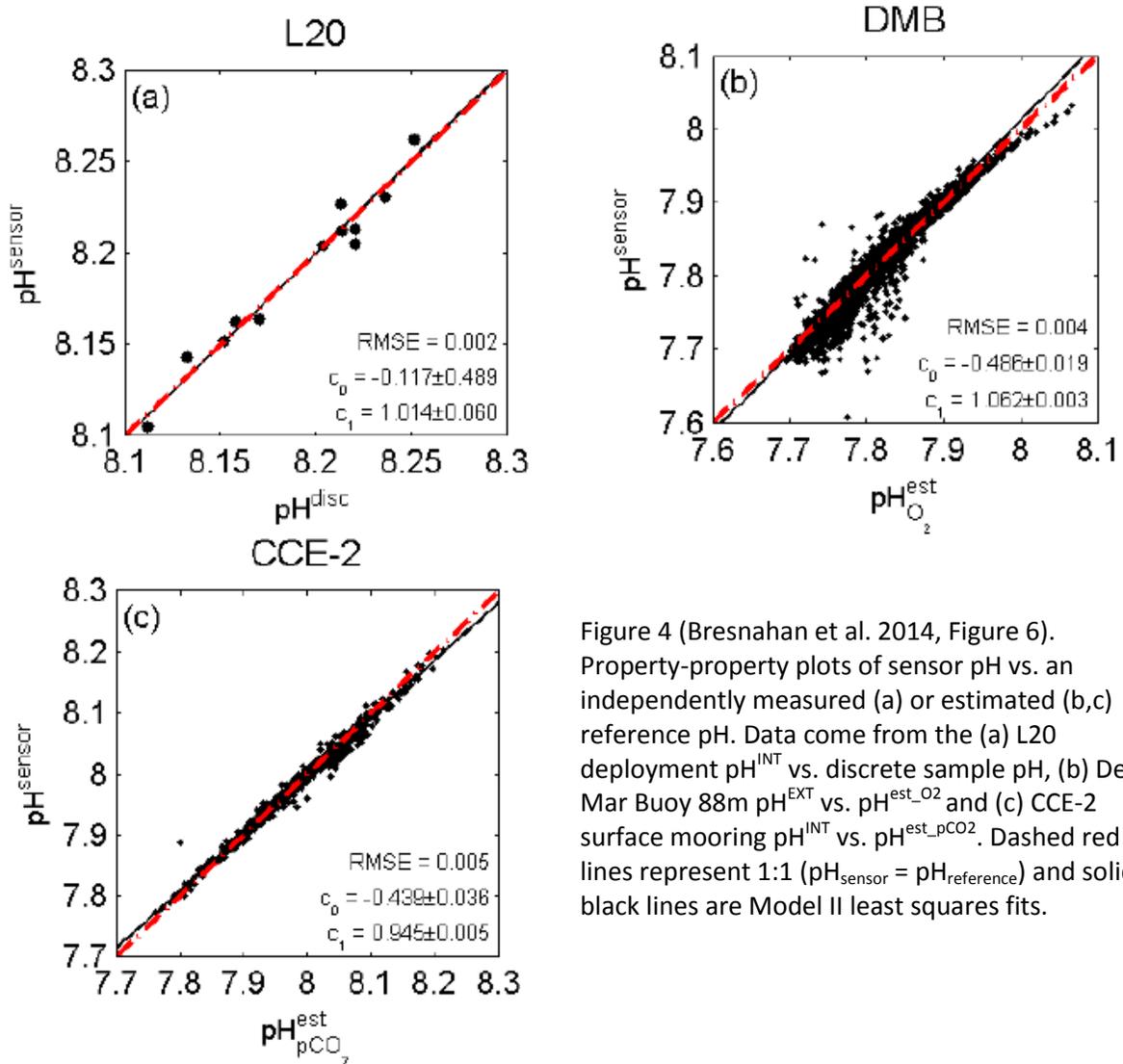


Figure 4 (Bresnahan et al. 2014, Figure 6). Property-property plots of sensor pH vs. an independently measured (a) or estimated (b,c) reference pH. Data come from the (a) L20 deployment pH^{INT} vs. discrete sample pH, (b) Del Mar Buoy 88m pH^{EXT} vs. $pH^{\text{est}_{O_2}}$ and (c) CCE-2 surface mooring pH^{INT} vs. $pH^{\text{est}_{pCO_2}}$. Dashed red lines represent 1:1 ($pH_{\text{sensor}} = pH_{\text{reference}}$) and solid black lines are Model II least squares fits.

Recommendation 9. Apply a single calibration point, chosen to minimize the anomaly relative to a trustworthy reference pH throughout the deployment. In particular, it is not recommended to force sensor data to agree with multiple individual bottle samples as this imparts sampling error to the sensor time series.

In addition to the pre-deployment calibration, we recommend incorporating validation samples into an ongoing sensor deployment. These samples serve to validate the pre-deployment calibration, identify sensor drift or failure, and potentially correct sensor data in the event of calibration drift.

Experience indicates that the Durafet remains stable over multiple months when deployed continuously in seawater. The Durafet sensors repeatedly demonstrate a 100% Nernstian response (Takeshita et al., 2014) and exhibit a stable and repeatable potential at a given temperature, salinity, and pH, with a highly linear and stable response to temperature across multiple sensors. This long-term sensor stability justifies a single-point calibration approach under most circumstances. The single-point calibration, specific to each reference electrode, defines the intercept (E_0) in a line of pH vs. sensor voltage at in situ calibration conditions. Thus, the calibration point is defined as a sensor voltage at a known pH, temperature, and salinity. Sensor voltages are extended over a range of pH, temperature, and salinity by assuming a 100% Nernst slope and a constant rate of change in voltage with temperature. For a thorough description of the various pH scales and inter-conversions, the reader is referred to Marion et al. (2011). Users are discouraged from forcing sensor data to agree with multiple individual bottle samples taken over the time course as this has been demonstrated to impart sampling error to the sensor time series. An in situ calibration point should be taken after period of initial conditioning (if conditioning of sensor was not conducted prior to deployment) and within the first week of deployment before any discernable sensor drift has occurred.

In physically and biogeochemically dynamic environments such as the nearshore, it can be challenging to capture synchronized discrete samples to set an accurate calibration constant. At the site where the data from Figure 5 were collected (MBARI L20 mooring), the SeapHOx sensors observed average pH changes of $0.023 \text{ pH}\cdot\text{hr}^{-1}$ but recorded instantaneous rates at least a full order of magnitude greater; thus, calibrating to a sample with even slight spatiotemporal mismatch in such an environment can introduce significant errors (Bresnahan et al. 2012). As opposed to using a single data point, Bresnahan et al., used a calibration constant for a SeapHOx which forced the mean difference between the sensor values and discrete values to be zero, thus minimizing the overall difference between sensor and discrete samples of pH. Figure 5 depicts the resulting offsets for each individual discrete measurement and the sensor value that results when E_0 is set using an average value to minimize the differences in pH between the internal and discrete pH measurements. This anomaly resulted from: (1) significant environmental pH gradients combined with small spatiotemporal mismatch between sensor and discrete sample and/or (2) errors in the discrete sample analysis. Analysis of the time-series suggested that spatiotemporal mismatch is the dominant control; in a dynamic near-shore ecosystem, a small sampling discrepancy could certainly contribute (unbiased) anomalies of this magnitude. The random anomalies in Figure 5 suggests that resetting the calibration constant to match each discrete value would impart an artificial variability in calculated pH with a magnitude of ~ 0.015 pH units and a frequency equal to the discrete sampling frequency. By choosing a single calibration constant based on multiple discrete samples, the error is substantially reduced.

In summary, best practices suggest first eliminating sensor data with identifiable drift using a time-series anomaly plot followed by correcting data to more reliable contemporaneous pH measurements. If and only if the reference pH is trustworthy, E_0 is calculated such that the average anomaly between sensor and reference is minimized.

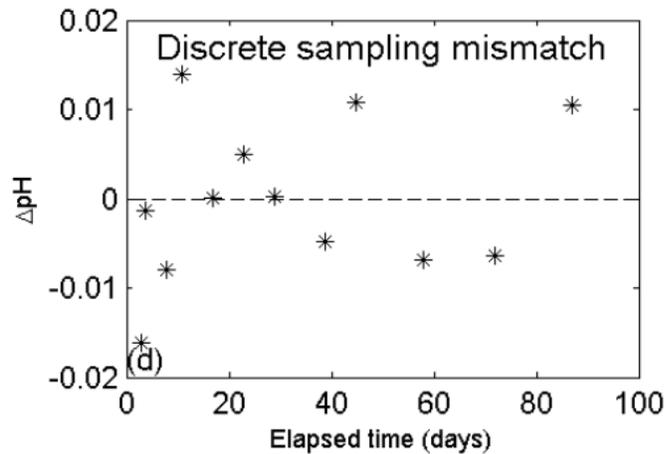


Figure 5 (From Breshahan et al, 2014, Figure 5d). Time series anomaly of difference between pH measured by the internal reference electrode pH^{INT} of a SeapHOx compared to independent, discrete measurements of pH measured in the laboratory using the *m*-cresol purple spectrophotometric method. Black dashed lines represent a zero anomaly.

Recommendation 10. Establish an error envelope for the sensor time-series. The accuracy of the sensor time-series can be no better than the reference to which it is calibrated or validated.

Without an estimate of the error associated with each of the measurements, comparisons of datasets across regions and time are meaningless. Thus, the final recommendation is to establish and report the error envelope for each sensor deployment. Report errors as RMSE between sensor and reference values.

Note 1: pH Scale

For data reporting purposes a pH scale must be specified. The pH is commonly calculated on the free, total (tot), and seawater (SWS) scales. A pH value, reported on a particular scale is converted to another scale as follows:

$$\begin{aligned} \text{pH}_{\text{tot}} &= \text{pH}_{\text{free}} - \log\left(1 + \frac{S_T}{K_S}\right) \\ \text{pH}_{\text{tot}} &= \text{pH}_{\text{SWS}} - \log\left(1 + \frac{S_T}{K_S}\right) + \log\left(1 + \frac{S_T}{K_S} + \frac{F_T}{K_F}\right) \\ \text{pH}_{\text{SWS}} &= \text{pH}_{\text{free}} - \log\left(1 + \frac{S_T}{K_S} + \frac{F_T}{K_F}\right) \\ \text{pH}_{\text{SWS}} &= \text{pH}_{\text{tot}} + \log\left(1 + \frac{S_T}{K_S}\right) - \log\left(1 + \frac{S_T}{K_S} + \frac{F_T}{K_F}\right) \\ \text{pH}_{\text{free}} &= \text{pH}_{\text{tot}} + \log\left(1 + \frac{S_T}{K_S}\right) \\ \text{pH}_{\text{free}} &= \text{pH}_{\text{SWS}} + \log\left(1 + \frac{S_T}{K_S} + \frac{F_T}{K_F}\right) \end{aligned}$$

where S_T , F_T , K_S , K_F are functions of temperature and salinity. Further details on these calculations may be found in (Riebesell et al., 2010) and recommended software programs include CO2SYS (Lewis and Wallace, 1998) and CO2calc (Robbins et al., 2010)

For ease of comparability, C-CAN recommends that all pH data be reported on the total scale.

Note 2: Data processing functions for sensors based on the Honeywell Durafet

The functions below are provided for users with access to raw voltages from Durafet-based sensors. Durafet users without access to raw voltages may still follow the recommended protocols listed above, by processing all data in the pH domain.

getDurafetTemp.m returns temperature (tempC, °C) from the Durafet's thermistor voltage (VTherm, V) when an independent conductivity/temperature sensor is not available. Note that Durafet thermistors are accurate to ± 0.5 °C, making it necessary to perform a calibration to a known reference temperature in order to retrieve an offset value (TCOffset, °C).

```
function tempC = getDurafetTemp(VTherm,TCOffset)
% Convert Durafet thermistor voltage to temperature (C) using following
polynomial
c0 = 340.9819863; c1 = -9.10257E-05; c2 = -95.08806667; c3 = 0.965370274;
RTherm = 20000./(3.3./VTherm-1);
tempC = c0+c1*RTherm+c2*log10(RTherm)+c3*(log10(RTherm)).^3;
tempC = tempC+TCOffset;
```

pHCalib.m has inputs of discrete E_{INT} (V), E_{EXT} (V), pH, temperature (°C), and salinity at time of calibration and returns the calibration coefficients $E_{INT,25}^*$ and $E_{EXT,25}^*$.

```
function calib = pHCalib(calEint,calEext,calpH,calT,calsal)
% Univ gas constant, Faraday constant,
R = 8.3145; F = 96487;
% Temperature dependence of standard potentials, Martz et al. 2010
dE0int = -0.001101; dE0ext = -0.001048;
% See Martz et al. 2010 for greater detail
tempK = calT+273.15; % Convert temp from C to K
S_T = (R*tempK)/F*log(10); % Nernst temp dependence
E0int = calEint-S_T*calpH; % Calc E0int from Nernst & pH @ calibration point
E0int25 = E0int+dE0int*(25-calT);
Z = 19.924.*calsal./(1000-1.005.*calsal); % Ionic strength, Dickson et al.
2007
SO4_tot = (0.14/96.062)*(calsal./1.80655); % Total conservative sulfate
cCl = 0.99889/35.453.*calsal/1.80655; % Conservative chloride
mCl = cCl*1000/(1000-calsal.*35.165/35); % mol/kg-H2O
K_HSO4 = exp(-4276.1/tempK+141.328-23.093*log(tempK)...
+(-13856/tempK+324.57-47.986*log(tempK))*Z^0.5...
+(35474/tempK-771.54+114.723*log(tempK))*Z-2698/tempK*Z^1.5...
+1776/tempK*Z^2+log(1-0.001005.*calsal)); % Bisulfate equilibrium
const., Dickson et al. 2007
pHint_free = calpH+log10(1+SO4_tot/K_HSO4);
cHfree = 10^(-pHint_free); % mol/kg-sw
pHint_free = pHint_free+log10((1000-calsal.*35.165/35)/1000); % mol/kg-H2O
mHfree = 10^(-pHint_free); % mol/kg-H2O
DHconst = 0.00000343*calT^2+0.00067524*calT+0.49172143; % Debye-Huckel, Khoo
et al. 1977
log10gamma_HCl = 2*(-DHconst*sqrt(Z)/(1+1.394*sqrt(Z)))+(0.08885-
0.000111*calT)*Z);
```

```

aHfree_aCl = mHfree*mCl*10^(log10gamma_HCl);
E0ext = calEext+S_T*log10(aHfree_aCl);
E0ext25 = E0ext+dE0ext*(25-calT);

```

```

calib = [E0int25 E0ext25];

```

pHCalc.m uses the calibration coefficients to calculate pH given the full E_{INT} , E_{EXT} , temperature, and salinity time-series. Note that the term $E0$ written in the code below is referred to as E^* in text and what is here written as E (e.g., E_{INT} , E_{EXT}) has often been referred to in its engineering units as V (V_{INT} , V_{EXT}).

```

function calc = pHCalc(Eint,Eext,E0int25,E0ext25,tempC,salt)
% Univ gas constant, Faraday constant,
R = 8.3145; F = 96487;
% Temperature dependence of standard potentials, Martz et al. 2010
dE0Int = -0.001101; dE0Ext = -0.001048;
% See Martz et al. 2010 for greater detail
tempK = tempC+273.15; % Convert temp from C to K
S_T = (R*tempK)/F*log(10); % Nernst temp dependence
pHint_tot = (Eint-(E0int25+dE0Int*(tempC-25)))/S_T; % Calc pHint from Nernst
Z = 19.924.*salt./(1000-1.005.*salt); % Ionic strength, Dickson et al. 2007
SO4_tot = (0.14/96.062).*(salt./1.80655); % Total conservative sulfate
cCl = 0.99889./35.453.*salt./1.80655; % Conservative chloride
mCl = cCl.*1000./(1000-salt.*35.165/35); % mol/kg-H2O
K_HSO4 = exp(-4276.1./tempK+141.328-23.093.*log(tempK)...
             +(-13856./tempK+324.57-47.986.*log(tempK)).*Z.^0.5...
             +(35474./tempK-771.54+114.723.*log(tempK)).*Z-
             2698./tempK.*Z.^1.5...
             +1776./tempK.*Z.^2+log(1-0.001005.*salt)); % Bisulfate equilibrium
const., Dickson et al. 2007
pHint_free = pHint_tot+log10(1+SO4_tot./K_HSO4); % free scale mol/kg-sw
DHconst = 0.00000343.*tempC.^2+0.00067524.*tempC+0.49172143; % Debye-Huckel,
Khoo et al. 1977
log10gamma_HCl = 2*(-DHconst.*sqrt(Z)./(1+1.394*sqrt(Z)))+(0.08885-
0.000111*tempC).*Z);
pHext_free = -(((E0ext25+dE0Ext*(tempC-25))-Eext)-
S_T.*(log10(mCl)+log10gamma_HCl))/S_T; % mol/kg-H2O
pHext_free = pHext_free-log10((1000-salt.*35.165/35)/1000); % mol/kg-sw
pHext_tot = pHext_free-log10(1+SO4_tot./K_HSO4);

calc = [pHint_tot pHext_tot];

```

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BBP Continuous Water Quality Monitoring Program Calibration Log



Station Name:

Sonde Code	Serial Number	Model Number	Nickname
Datasonde: <input style="width: 175px; height: 20px;" type="text"/>	<input style="width: 155px; height: 20px;" type="text"/>	<input style="width: 145px; height: 20px;" type="text"/>	<input style="width: 235px; height: 20px;" type="text"/>
Comments: <input style="width: 585px; height: 40px;" type="text"/>			Description <input style="width: 235px; height: 40px;" type="text"/>

DATASONDE MAINTENANCE

Date of Calibration: <input style="width: 100px; height: 20px;" type="text"/> mm/dd/yyyy	Technicians: <input style="width: 240px; height: 20px;" type="text"/>
Batteries Installed: <input style="width: 100px; height: 20px;" type="text"/>	DO/ODO membrane replaced: <input style="width: 240px; height: 20px;" type="text"/>

PRE-DEPLOYMENT CALIBRATION

Pre-Deployment	Sensor Diagnostics	Programming																																																																											
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Turbidity <input type="checkbox"/>																																																																													

Comments-Pre:

DEPLOYMENT INFORMATION and FIELD LOG

Date Deployed: Time: Technicians: White Towel:

Field Data:

Water Temp: <input style="width: 120px; height: 20px;" type="text"/> °C	DO Conc.: <input style="width: 120px; height: 20px;" type="text"/> mg/L	pH: <input style="width: 120px; height: 20px;" type="text"/>
Barometric Pressure: <input style="width: 120px; height: 20px;" type="text"/> mmHg	Sp. Cond: <input style="width: 120px; height: 20px;" type="text"/> µm	pH mV: <input style="width: 120px; height: 20px;" type="text"/>
DO %: <input style="width: 120px; height: 20px;" type="text"/> %	Salinity: <input style="width: 120px; height: 20px;" type="text"/> psu	Instrument: <input style="width: 120px; height: 20px;" type="text"/>

In Field Maintenance: Note changes to site during deployment, sonde tube maintenance, biofouling removal, etc.

Date: Duration: White Towel:

Comments:

BBP Continuous Water Quality Monitoring Program Calibration Log



Station Name:

RETRIEVAL INFORMATION FIELD LOG

Date Retrieved: Time: Technicians: White Towel:

Field Data:

Water Temp: °C DO Conc.: mg/L pH:
 Barometric Pressure: mmHg Sp. Cond: pH mV:
 DO %: % Salinity: psu Instrument:

In Field Maintenance: Note changes to site during deployment, sonde tube maintenance, biofouling removal, etc.

Date: Duration: White Towel:

Comments:

Fouling Presence:

Type: A=algae, B=barnacles, C=crabs, E=eggs, F=fish, H=hydroids, MD=mud, S=sponges, SI=silt, SL=shell, SP=shrimp, T=tunicates, W=worms, O=other, N=none

Amount: H=heavy, M=moderate, L=light (e.g. A/H, B/L)

Sonde/Guard: Dissolved Oxygen:
 Temp/Cond: Turbidity:
 pH: Wiper/Brush:

Comments:

POST-DEPLOYMENT CALIBRATION

Post-Deployment

	<u>Sonde</u>	<u>YSI</u>
Temp	<input style="width: 80px;" type="text"/> °C	<input style="width: 80px;" type="text"/> °C
Optical %DO @ 100% sat	<input style="width: 80px;" type="text"/> %	<input style="width: 80px;" type="text"/> %
Baro. Pres. (Depth Calib)		<input style="width: 80px;" type="text"/> m
Depth 0.0 offset	<input style="width: 80px;" type="text"/> m	

	<u>Sonde</u>	<u>Standard</u>
SpCond	<input style="width: 80px;" type="text"/> mS/cm	<input style="width: 80px;" type="text"/> mS/cm
pH7	<input style="width: 80px;" type="text"/>	<input style="width: 80px;" type="text"/>
pH 10	<input style="width: 80px;" type="text"/>	<input style="width: 80px;" type="text"/>
pH 4	<input style="width: 80px;" type="text"/>	<input style="width: 80px;" type="text"/>
Turb	<input style="width: 80px;" type="text"/> NTU/FNU	<input style="width: 80px;" type="text"/> NTU/FNU
Turb	<input style="width: 80px;" type="text"/> NTU/FNU	<input style="width: 80px;" type="text"/> NTU/FNU
Battery voltage	<input style="width: 80px;" type="text"/> v	(remove ext. power -650,6038)

Sensor Diagnostics

pH 7 (0 +/- 50mV)	<input style="width: 80px;" type="text"/>	Calculated pH slope (4/7 will result in negative slope)	4...7	<input style="width: 80px;" type="text"/>
pH 10 (-180 +/- 50 mV)	<input style="width: 80px;" type="text"/>		7...10	<input style="width: 80px;" type="text"/>
pH 4 (+180 +/- 50mV)	<input style="width: 80px;" type="text"/>		0	<input style="width: 80px;" type="text"/>
Calculated pH slope (4/7 will result in negative slope)	4...7	<input style="width: 80px;" type="text"/>		
	7...10	<input style="width: 80px;" type="text"/>		

Comments-Post:

