Ocean and Coastal Acidification Monitoring in Casco Bay

Casco Bay Estuary Partnership
Quality Assurance Project Plan (DRAFT)

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This QAPP is effective for a period of one year from EPA approval date

A. Program Management

A1 Approval Page

U.S. Environmental Protection Agency Region 1

8/9/16

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Quality Assurance Unit
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A2 Table of Contents

A3 Distribution List

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In addition, this QAPP will be distributed to Dr. Brian Tarbox, Southern Maine Community College, Michael Doan Friends of Casco Bay (FOCB) and Brian Rappoli, EPA Headquarters.

A4 List of Acronyms

CBEP	Casco Bay Estuary Partnership
CO_2	Carbon Dioxide
DegC	Degrees Celsius
DDW	Distilled/Deionized water
DIC	Dissolved Inorganic Carbon
EPA	Environmental Protection Agency
FOCB	Friends of Casco Bay
ISMN	Integrated Sentinel Monitoring Network

NEP	National Estuary Program
NECAN	Northeast Coastal Acidification Network
NERACOOS	Northeast Regional Association of Coastal Ocean Observing Systems
NOAA	National Oceanic and Atmospheric Administration
NROC	Northeast Regional Ocean Council
OPAL	Ocean Process Analysis Laboratory
PI	Principal Investigator
QA/QC	quality assurance and quality control
SAMI-CO_2	Submersed Automated Monitoring Instrument for pCO_2
SeaFET	Satlantic Field Effects Transistor
SMCC	Southern Maine Community College
SOP	Standard Operating Protocol
TA	Total Alkalinity
UTC	Universal Time Coordinated
UNH	University of New Hampshire
USM	University of Southern Maine

A5 Project/Task Organization

The following individuals or laboratories will carry out major responsibilities for the project's activities.

Curtis Bohlen, Executive Director, CBEP:
Provides funding, contract management, and advice on interpretation of data. Will oversee storage of final data on USM computers.

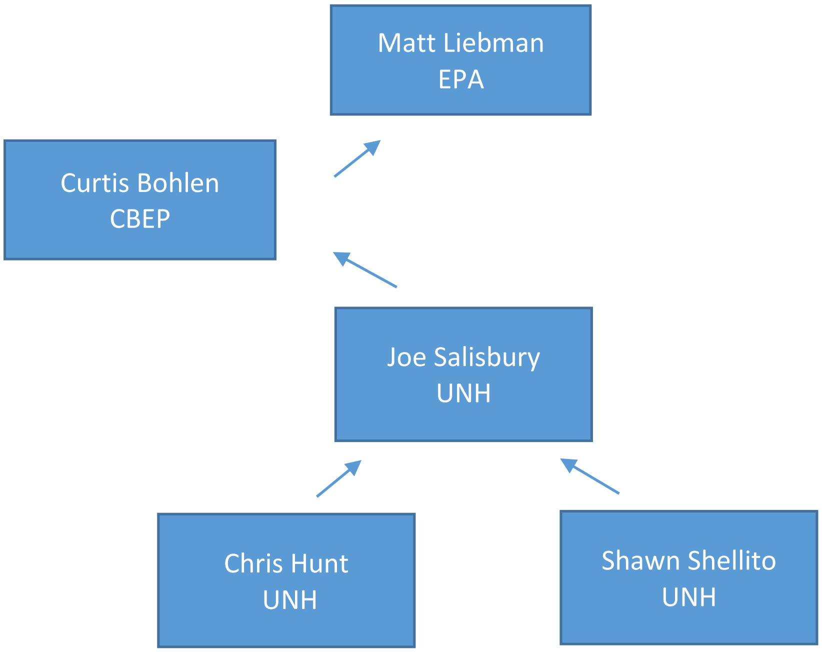
Joseph Salisbury, Associate Research Professor, Ocean Process Analysis Laboratory (OPAL) UNH:
Responsible for fabrication, installation and maintenance of sensor package, routine recovery of data, temporary data archiving, preliminary data interpretation, reporting on results to CBEP and EPA.

Chris Hunt, Research Scientist, OPAL, UNH:
Responsible for data processing and basic analysis, QA/QC, discrete sample analyses, training and supervision of undergraduate students for sample analysis of total alkalinity (TA) and dissolved Inorganic carbon (DIC).

Shawn Shellito, Research Scientist, OPAL, UNH:
Fabrication of sensors, sensor deployment, maintenance, recalibration, bottling sampling, initial processing of Sunburst sensors.

Brian Tarbox, Associate Professor, SMCC:
Assists with maintenance of SMCC pier including davit, secures access box, and uses data for students in SMCC marine science classes.

Figure A.1 Organization Chart



Curtis Bohlen is the overall Project Manager for this project and will report annually to EPA as part of annual reporting requirements of National Estuary Program (NEP) grants. Joseph Salisbury is the Principal Investigator and reports directly to Curtis Bohlen for this project. Chris Hunt and Shawn Shellito report directly to Joseph Salisbury for this project. Undergraduate students (work study for sample analyses, not shown) report directly to Chris Hunt.

A6 Problem Definition

Rising atmospheric CO_2 concentrations have increased the absorption of CO_2 in the ocean, where a chemical reaction that reduces the pH and makes the oceans more acidic occurs.

While ocean acidification is largely driven by atmospheric inputs, recent research indicates that acidification in coastal areas can be significantly altered by local processes including upwelling, riverine discharge, nutrient loading, hypoxia, organic carbon remineralization, and productivity. A more acidic ocean will adversely affect the health of many marine species, including plankton, mollusks, and other shellfish. On the east and west coasts of the United States, there already is evidence that economically important shellfish industries are being affected, because shellfish larvae are unable to form shells (and perish) in the acidic sea water. Indeed, EPA, and states, are in need of additional monitoring information to evaluate whether coastal acidification impairs aquatic life from a water quality standards perspective.

In response to this growing problem, in 2013 the Northeast Regional Association of Coastal and Ocean Observing Systems (NERAACOOS) helped establish the Northeast Coastal Acidification Network (NECAN). NECAN is a network of scientists, federal and state agency representatives, resource managers, and affected industry partners dedicated to coordinating and guiding regional observing, research, and modeling efforts. The purpose is to better identify critical vulnerabilities, particularly with respect to regionally important and economically significant marine resources. NECAN is part of the larger, joint project of NERACOOS and the Northeast Regional Ocean Council (NROC) to develop an Integrated Sentinel Monitoring Network (ISMN) for Climate Change in Northeastern Marine and Estuarine Ecosystems.

EPA Region 1 leveraged its involvement with NECAN to expand monitoring capacity in New England. EPA Region 1 and Casco Bay Estuary Partnership (CBEP) secured additional funding ($65,000 in Federal Fiscal Year 2014, starting July 2014 and $20,000 in Federal Fiscal Year 2015 starting July 2015) from the Office of Water to add to the annual CBEP base grant to establish and maintain a coastal acidification monitoring station in Casco Bay. For Federal Fiscal Year 2016, CBEP has dedicated additional funding ($10,000) from its annual EPA base budget to maintain the site. Scientists from UNH, CBEP, Friends of Casco Bay, and Southern Maine Community College (SMCC) scoped out a site for deployment of coastal acidification sensors at a pier on the SMCC campus in South Portland, ME. The site appears to have many of the characteristics necessary to detect a coastal acidification impact: it receives influences from fresh and salt water, has a moderate nutrient impact due to its urban setting, and is located near an existing, relatively stable eelgrass bed. CBEP has contracted with UNH to operate the site, and students from SMCC will help maintain the instruments. The hope is that station could become a long-term Casco Bay “observatory” and part of a growing network of coastal acidification monitoring stations associated with NECAN and with a Casco Bay monitoring network.

The Office of Water is interested in assisting states protect designated uses -- such as propagation and harvesting of shellfish -- that are impacted by ocean and coastal acidification. States are required to assess waters for impairment to shellfish harvesting or aquatic life and EPA has committed to providing guidance on how to conduct these assessments.[1] Although laboratory experiments document impacts to larval and adult shellfish, there is insufficient data in the field to classify waters as impaired or threatened due to ocean and coastal acidification (Gledhill et al., 2015). One of the most important indicators of biological impacts is calcium carbonate saturation, and this can be easily calculated by measuring key carbon cycle parameters (described below). In order to make these linkages, then, it is necessary to better understand the current conditions in potentially impacted as well as unimpacted areas. This Casco Bay OCA observatory is one of a growing number of sites that will begin to make these assessments.

A7 Project Description and Schedule

The purpose of this project is to install continuous monitoring sensors in Casco Bay to measure at a high temporal resolution ocean and coastal acidification parameters. In addition to pH, the parameters that are important biologically relate to calcium carbonate mineral saturation state (also called "omega"). Saturation of calcium carbonate (as aragonite or calcite) can be calculated by a combination of two of the four master carbon cycle parameters: pH; carbon dioxide (CO_2); total alkalinity (TA); and dissolved inorganic carbon (DIC). Calculation of saturation is also dependent on temperature and salinity conditions.

To calculate omega, UNH has installed four instruments:

- Satlantic SEAFET pH sensor (owned by CBEP);
- Sunburst Submersed Automated Monitoring Instrument (SAMI) for CO_2 (owned by UNH);
- Aanderaa Optical Oxygen Optode sensor (owned by CBEP); and
- Seabird conductivity (salinity) and temperature sensors (owned by UNH).

Omega will be calculated on an hourly basis using an MS-Excel computer software package called CO2SYS that is based on dissociation constants of carbonic acid (Lewis and Wallace, 1998). Using simultaneous measurements of pH, pCO2, temperature, and salinity, CO2SYS calculates aragonite and calcite saturation state, as well as total alkalinity and dissolved inorganic carbon. <u>To provide validation of the in situ instruments</u>, bottle samples are collected every four to six weeks for laboratory analyses for TA and DIC and used to back calculate estimated pH and pCO2 (described in section B5). The process is illustrated in Figure A.2 below.

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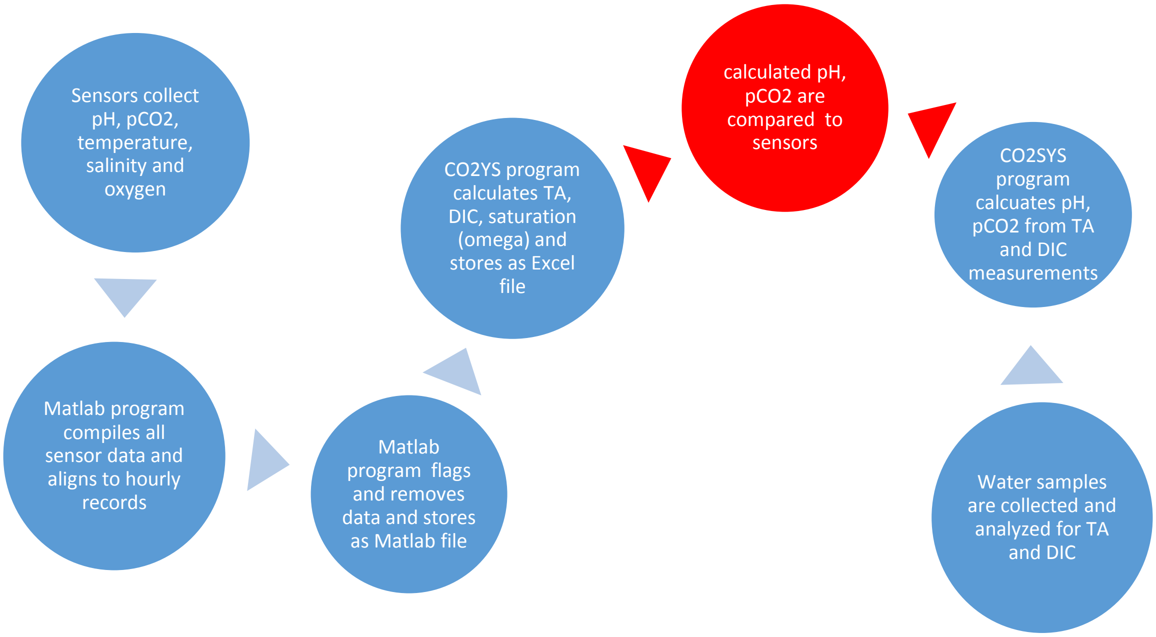
[1] Memorandum from Denise Keehner, Office of Water to Water Division Directors on Integrated Reporting and Listing Decisions Related to Ocean Acidification, November 15, 2010.

Figure A.2 Sensor data processing and validation to bottle samples.



The system is installed at the Southern Maine Community College (SMCC) pier in South Portland, Maine. The pier is located in the Portland Channel, an important southern outlet of Casco Bay, and near outlets of the Fore and Presumpscot rivers in a relatively urban area of Casco Bay. This location was selected because it is nearshore, accessible, and has historic nutrient data collected by the Friends of Casco Bay.

The sensors have been installed by Joseph Salisbury and his staff at UNH. UNH built a cage to house the sensors. The cage is attached via a davit within a secure box at the pier in about 1 to 5 meters of water (depending on tide). The cage rests on the bottom and the sensors are about ½ meters off the bottom and always submerged.

Sensors were deployed in April 2015 (as a trial deployment) and will be operational through 2016 and (most likely, if funding available) 2017. Every 4 to 6 weeks the system is retrieved and data is downloaded in text format and converted to excel. Each instrument produces a time stamp and data stream.

The data cannot be served in real time, because the power and dock at SMCC does not have this capability at this time. We hope to establish that in the future. We plan to integrate the data into the NERACOOS data architecture as well.

The data will be recorded in hourly increments and reported in the units listed in Table A.1.

Table A.1 Parameters and units reported

Parameter	**Units**
pH	pH Total scale
pCO_2	μatm
Dissolved oxygen	μmol/l converted to μmol/kg
Conductivity (salinity)	μSiemens/cm converted to salinity
Temperature	degrees Celsius
Total Alkalinity	μmol/kg
Dissolved Inorganic Carbon	μmol/kg

* Note that oceanographic convention is moving towards replacing parts per thousand and practical salinity units with salinity as a unitless quantity. Salinity is derived from conductivity.

Deliverables for this project are listed below in Table A.2

Table A.2 Work Products and Deliverable Schedule

Work Product/Deliverables	**Schedule**
First year installation	April 2015
Progress reports and data update	Semiannually during the first year
First year data and data report	May 4, 2016
Draft QAPP	November 1, 2015
Second year installation	June 2016
Final QAPP	August 1, 2016
Progress reports and data update	Semiannually during the second year
Final data submission and report	June 2017
Potential Third deployment	April 2017 if funding available

A8 Quality Objectives and Criteria

Methods and performance specifications are provided for field instruments. Because none of these parameters have regulatory limits, there are no project action levels. The following instrument data quality indicators are partly based on instrument manuals and specification datasheets listed in Appendix A.

Table A.3 Data quality indicators for instruments

Parameter	Method/Instrument	Range	Accuracy	Precision/Resolution
pH	SeaFET pH sensor is an ion-sensitive field effect transistor (ISFET).	6.5 to 9.0 pH	0.02 pH	0.004 pH
CO_2	Colorimetric SAMI Sunburst CO_2	150 to 1000 µatm	+/- 3 µatm	±0.5 - 1 µatm
Dissolved oxygen	Aanderaa Oxygen Optode	0-500 µmol/l	<8 µmol/l	<1 µmol/l
Conductivity (salinity)	Sea-Bird Electronics SBE-37	0-70 µS/cm	0.003 µS/cm	0.0001 µS/cm
Temperature	Sea-Bird Electronics SBE-37	-5-45 degC	0.002 degC	0.0001 degC

Reporting Limits and Ranges
Instrument reporting limits are determined by the range and precision of the sensors being used and are provided by the manufacturers of the instrument sensors which provide annual calibration.

Accuracy
Accuracy measures how close results are to a true or expected value and can be determined by comparing a standard or reference sample to its actual value. All instruments are returned to the manufacturer on an annual basis for calibration using reference values and analytical instrumentation. Laboratory grade instruments are used from bottle samples to validate the *in situ* sensor measurements.

Precision

With the described methods we have limited capability to assess precision of the sensor measurements and are relying on the precision reported by the manufacturers of the instruments. We cannot adequately evaluate field precision (i.e. we cannot perform field duplicates) because we only have one instrument per parameter and repeated measurements will vary depending on water conditions. However, some of the instruments are set to record in bursts (SeaFET) or every ten minutes (Sea-Bird) so statistics for repeated measurements (e.g. mean, median, minimum, maximum and standard deviation) are automatically calculated and can be reviewed if necessary.

Bias/Drift

Bias or drift is a measurement of correctness and includes components of systemic error. A measurement is considered unbiased when the value reported does not differ from the true value. For the SAMI, internal periodic blanks are automatically run to correct for drift of the electro-optical system, while reference measurements of the LEDs correct for interim deviations. Instruments are inspected, maintained and cleaned periodically to contain drift caused by biofouling or other factors.

Representativeness

Representativeness is a measure of how accurately a monitoring program reflects the actual water quality conditions. Data collected under this QAPP will be considered representative of ambient water quality conditions of inner Casco Bay and will be measured over multiple years. Results will be compared to other monitoring program results (see section C2) for similar parameters to evaluate representativeness.

Comparability

The comparability of the data produced is partly determined by the commitment of the staff to use only approved procedures as described in this QAPP. Comparability is also guaranteed by reporting data in standard units, by using accepted rules for rounding figures, and by reporting data in a standard format.

Completeness

The completeness of the data is a relationship of how much of the data is available for use compared to the total potential data. Ideally, 100% of the data should be available. However, the possibility of unavailable data due to biofouling, routine maintenance for optimal sensor functions, and unexpected sensor failure (e.g. battery failure) can be expected. Therefore, it will be a general goal of the project that a data collection rate of 70% or higher will be achieved, a reasonable expectation due to instrumentation challenges. This rate should allow for robust interpretation of the dataset depending on the nature of the scientific hypotheses.

In sum, sensor data will be assured by:

- factory and laboratory instrument calibrations;
- validation to water quality measurements;
- inspection of the data record for anomalous data;
- proper maintenance and examinations for bias and fouling;
- checks against oceanographic properties and other programs' data; and
- electronic data validation and verification.

A9 Special training and certifications

Joseph Salisbury, the UNH Principal Investigator is considered a national expert on carbon chemistry and has over 40 peer reviewed publications in the last ten years in this field. OPAL Research scientists Chris Hunt (M.S) has 10+ years' experience collecting and analyzing TA and DIC samples and Shawn Shellito (M.S.) has 10+ years of instrument deployment experience in the Gulf of Maine. Chris Hunt is working on his Ph.D. and keeps up to date with current methodologies and progress in the area; he recently attended an analysis workshop hosted by Dr. Andrew Dickson (world pH expert) at Scripps Marine Lab in San Diego, CA.

OPAL Laboratory personnel (undergraduate lab technicians) are trained in instrument calibration procedures, data quality acceptability, and data processing procedures by Chris Hunt. Certified Reference Materials are used to check measurement quality for TA and DIC. Chris Hunt directly supervises personnel during an initial training period until correct instrument operation is ensured, and periodically checks data quality. Laboratory personnel typically have experience in the laboratory of two or more years. Lab output is typically 50 to 75 samples per month from a diverse set of oceanographic projects.

A10 Documents and records

The documents that describe, specify, report, or certify activities, requirements, procedures, or results for this project and the items and materials that furnish objective evidence of the quality of items or activities are listed in Table A.4. The Project PI will be responsible for assuring that all project personnel have the most recent version of the QAPP, any amendments to the QAPP and any updates. Timely communication via email or telephone or in person with personnel listed in Section A3 will be done to ensure both EPA and CBEP staff have most recent version of

QAPP. The PI will ensure that instrument operator manuals and standard operating protocols (SOPs) are up to date and available during the period of the project.

During the project, it is possible that changes will occur and amendments or revisions to the QAPP may be required. Revisions may be necessary to reflect changes in project organization, tasks, schedules, objectives, and methods; address deficiencies and nonconformance; to improve operational efficiency; and/or to accommodate unique or unanticipated circumstances. Requests for Amendments/Revisions will be made by CBEP to EPA in via email. Any changes that significantly affect the technical and quality objectives of the project will require a revision and re-approval of the QAPP, and a revised copy will be sent to all persons on the distribution list.

Table A.4 Document and record retention information.

Document/Record	Location	Retention	Form
QAPP	UNH, CBEP, EPA	Duration of Grant	Paper/electronic
Field notebooks	UNH	Duration of Grant	Paper
Laboratory notebooks	UNH	Duration of Grant	Paper
Laboratory SOPs	UNH	Duration of Grant	Paper/electronic
Corrected sensor data	UNH, CBEP	Duration of Grant	
Annual Report with data interpretation	UNH, CBEP	Duration of Grant	Paper/electronic
Final Report with data interpretation	UNH and CBEP	Duration of Grant	Paper/electronic

B. Measurement and Data Acquisition

B1 Automated sensors process design

It is expected that all sensors will work continuously for one year during the early summer to early winter time period each year. The sensors will be temporarily (for less than two hours) removed approximately every 4 to 6 weeks for on-site data download, maintenance, and discrete sample collection. In the early winter (December to January), the sensors will be removed from the site for maintenance and calibration and sent to manufacturer for calibration.

If an unexpected event happens, such as sensor malfunction, corrective procedures will be taken including diagnosis under the direction of the manufacturers of the instruments.

Sensor data are designed to record on an hourly basis. This was based on evaluating a tradeoff between battery storage, data storage and ambient variability. Sensors clocks synch to the laptop UTC (universal time coordinated) computer clock when launched or connected. The laptop automatically updates when online. UTC is very precise and may drift a second or two per month.

The SeaFET is set to record on an hourly basis on the half hour. To capture the high frequency variance in the pH signal we collect 30 to 50 non-averaged frames per measurement and averaged to one sample. The burst of data takes approximately 10 hz (so there are about 30 to 50 measurements in 3 to 5 seconds)

The SAMI-$CO_2$is also set to conduct a cycle every hour on the half hour. It collects one optical absorbance measurement per sample to derive pCO_2.

The Aanderaa oxygen optode reads immediately after the SAMI-CO_2 measurement.

The Sea-Bird instruments record every 10 minutes and the average value for that hour is recorded.

The data processing procedure aligns all data to an hourly measurement as described in Appendix B and creates a text file for further analysis.

B2 Water Sampling Methods

To validate the sensors, UNH scientists collect ambient water at the sensor deployment site for TA and DIC during data recovery efforts (see Appendix C for UNH water sampling protocol). Sampling is typically (but not always) at high tide to avoid resuspension of sediments into the water column during recovery of the instrument package. Water samples are collected with a Niskin bottle 0.5m above the bottom, at the height of the sensor position. Samples are immediately transferred to a pre-labelled 120 ml (or sometimes a 60 mL) glass bottle with a stopper, ensuring no bubbles or headspace is present. The samples are preserved with two drops of saturated mercuric chloride. Field duplicates are prepared from each Niskin bottle.

A field notebook is used to record ambient and weather conditions. No chain of custody form is filled, but samples are clearly labeled with site name, time and date, and if duplicates were collected. Using the date and time, the Sea-Bird C/T sensor data are searched for the corresponding salinity and temperature for the time of the sample. The salinity and temperature measurements, along with the TA and DIC measurements are recorded in a spreadsheet and processed using CO2SYS to calculate derived pH and pCO_2 (see below).

B3 Water Sample Handling and Custody

The bottle samples for TA/DIC are preserved with mercuric chloride and then refrigerated until time of analysis at 4 degrees Celsius. The holding time is up to six months (although with preservation by mercuric chloride, it is assumed that holding time is up to two years[2]).

B4 Laboratory Analytical Methods

Water samples are analyzed for TA and DIC within six months (see Appendices D and E for the methods for the TA and DIC analyses respectively).

B5 Quality Control for Instruments

UNH technicians will adhere to manufacturer's guidelines in the preparation all the sensors for field deployment and service. In the event of a discovery of a failure to comply with established quality control procedures, corrective actions will be made upon determination of the point of the failure. Should the failure be in the electronic process, repair or replacement of the suspected component(s) will be warranted. If the failure is due to faults of personnel, corrective action will be reinforcement of training. Equipment problems will be documented in a field notebook, and the PI will be notified upon the discovery of such problems, corrective actions taken, and final outcome.

Every four to six weeks, sensor data are downloaded directly to a laptop computer. All sensor data will be subject to QA/QC within one week of retrieval.

SAMI-CO_2 time series data are examined on-site to determine that measurements are within manufacturer specified range. CO_2 blank measurements are also checked on-site to examine instrument drift. If CO_2 data on-site are shown to be problematic, according to blank measurements, the sensor is brought back to UNH and data are returned to the instrument manufacturer (Sunburst) for additional processing and recovery. The manufacturer may

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[2] Dr. Jason Grear, Atlantic Ecology Division, personal communication

recommend that the data are not suitable, or that the sensor needs to be returned for recalibration or repair.

All data are returned to UNH after recovery as individual text (.txt) files. Matlab code at UNH is run to match up individual sensor data on an hourly time-step, calculate hourly statistics (mean, median, minimum, maximum, and standard deviation), flag questionable data, and calculate omega, TA and DIC estimates from observed temperature, salinity, pH and pCO_2 (see Appendix B for Casco Bay data processing steps).

Data will be flagged if they are:

- Beyond the measurement ranges;
- Beyond expected values for Casco Bay estuary;
- Inconsistent with biogeochemical dynamics or trends (i.e. inversely varying oxygen and pCO2); or
- Unrealistically variable over hourly or daily time scales, beyond the bounds of reasonable environmental variation (noisy).

Temperature will be compared among two instruments (SAMI-CO_2 and Sea-Bird) and significant discrepancies will be flagged.

The PI prepares time series and property-property plots (e.g. pCO2 vs. pH) or DO vs. salinity to determine whether unusual oceanographic patterns exist.

The SeaFET measures a burst of 30-50 frames of data once per hour. This burst happens over a second or two, so it is really one instantaneous measure of the environment. The statistics of all the frames measured within the burst are recorded, and can be evaluated if other flags are identified.

Laboratory grade instrument analyses (Appendices D and E) are used from bottle samples to validate the *in situ* sensor measurements. Bottle samples are collected for laboratory analyses for total alkalinity and dissolved inorganic carbon and these data, together with temperature and salinity from the Seabird sensors, can be used to estimate pH and pCO_2 using dissociation constants of carbonic acid and computer software packages (CO2SYS; Lewis and Wallace, 1998). (Omega is also derived from the CO2SYS program.) These estimates can be used together with best professional judgement to assess sensor data quality and stability.

Accuracy of laboratory instruments for analysis of TA and DIC are ensured using calibration from certified reference material (CRM, Dickson *et al.*, 2003).

B6 Instrument/Equipment Testing, Inspection and Maintenance

All instruments (SeaFET, SAMI, Aanderaa, and Sea-Bird) are returned annually to manufacturer for internal calibration and service. When returned to UNH after calibration, all instruments are shipped with a verification checklist documenting calibration and other maintenance tasks. All instruments are checked for performance and internal clocks are synched to UTC.

To protect against bias caused by signal drift or biofouling, UNH will clean and maintain the sensors and perform validations using laboratory analyses for total alkalinity and dissolved inorganic carbon. Every four to six weeks during data recovery, the sensors are cleaned. The SeaFET transistor tip is wiped clean with a wet soft sponge using seawater (the SeaFET cannot come into contact with DDW). The SAMI internal cell and reservoir is flushed with externally supplied distilled/deionized water (DDW). The Optode foil is wiped and rinsed with DDW. The SBE-37 conductivity/temperature cell is flushed with DDW.

An antifouling copper shield is placed over the sensors to reduce potential for biofouling that could cause instrument drift or malfunction.

B7 Instrument Calibration and Frequency

The SeaFET pH sensor, SAMI-CO_2 and sensors do not recommend end-user calibration as the manufacturers pre-calibrate and provide calibration coefficients saved in the instruments prior to shipment. Within the lifetime of these sensors, both sensors will be shipped back to manufacturer for annual maintenance or recalibration to ensure optimal instrument performance.

For example, the SeaFET is calibrated at the Satlantic facility using a single-point calibration at 0.5m depth with spectrophotometric pH determination and the calibration coefficients are stored on the instrument. User manuals in Appendix A provide additional information.

The Aanderaa Optical Oxygen Optode is also calibrated annually in-house at 0 and 100% oxygen saturation.

The Laboratory instruments for TA and DIC are calibrated daily when in operation. For TA, a Certified Reference Material (CRM) of titration acid (also known as the “Dickson” standard) is run on a daily basis and the pH electrode is calibrated against three concentrations (See Appendix D). For DIC, a four point calibration curve against a Dickson DIC standards are run daily, and standards are run throughout the day (See Appendix E).

B8 Inspection/Acceptance of Supplies and Consumables

The laboratory manager of UNH (Chris Hunt) is responsible for ordering and receiving necessary chemical reagents, including CRM seawater from Dr. Andrew Dickson (Scripps/UCSD). Upon arrival, inspection of packaging will be done to ensure there are no broken CRM bottles. Certified information on TA and DIC of each CRM batch is provided on CDIAC website (http://cdiac.ornl.gov/oceans/Dickson_CRM/batches.html) and will be maintained there indefinitely. CRM can be stored at room temperature in the dark.

B9 Data Management

After data processing and review of sensor data for quality control, final spreadsheets will be saved and distributed to CBEP and EPA for data storage. Each spreadsheet will have headers including units as well as a tab for metadata. The spreadsheets will also include calculations for omega, TA and DIC based on the sensor results.

Results of discrete water samples before and after each field maintenance will be saved in the respective lab notebook for TA and DIC. Laboratory technicians will transcribe these sheets to a central Excel spreadsheet. Project-specific TA and DIC data will then be compiled into a single Excel spreadsheet and used for comparison to sensors. Laboratory TA/DIC data, however, will not be shared with CBEP since they are only used for quality control and not for reporting.

For the duration of the project, data (after QA/QC) will be saved on a UNH desktop computer (operated by Chris Hunt) which is routinely backed up through a cloud-based storage system (operated by Box.com). UNH will share the data with both CBEP and EPA staff. Long-term data will be housed at CBEP on a network drive owned by USM. One of the goals of the revised Casco Bay Plan (http://www.cascobayestuary.org/planning-for-casco-bays-future/) is to "standardize systems for collecting targeted Casco Bay information; providing ready access to stored information; and sharing it with allied organizations and their constituencies" (Action 4.1a). These data will be part of the CBEP project to store, distribute and interpret CBEP and Casco Bay-related environmental data. Also, data may be potentially shared with NERACOOS, although that organization is presently focused on providing real-time data. Data will also be shared with Brian Tarbox at SMCC for use as an oceanographic teaching tool.

C. ASSESSMENT/OVERSIGHT

C1 Assessments and Response Actions

The PI reviews the data using property-property plots for expected oceanographic relationships to determine data acceptability. Problems are returned to Chris Hunt for correction or removal. The PI will also review flagged data. All problematic data are flagged as Questionable.

The data will also be compared, where appropriate, to other OCA data being collected in Casco Bay or in Maine, include that collected by Friends of Casco Bay, Bowdoin College and The Island Institute. CBEP and UNH are participating in a nascent collaborative of research institutions called the Casco Bay Monitoring Network, which seeks to better coordinate monitoring activities in Casco Bay as part of the Casco Bay Plan.

C2 Reports to Management

Periodically CBEP or EPA staff will attend and observe retrieval of data and maintenance of sensors. Any observations that are inconsistent with the QAPP will be flagged.

UNH will prepare an Annual Project Report for CBEP which summarizes UNH activities for the annual project period including a description and documentation of major project activities; problems with performance of the sensors if any, evaluation of the project results, scientific interpretation; comparison to data quality indicators; description of questionable data if any, and a conclusion. Some of the data will be compared to other similar data gathering efforts in Casco Bay, including those by Friends of Casco Bay, Bowdoin College, and The Island Institute.

In addition to the electronic data, the annual reports will present the observed and calculated (i.e. omega) data as a time series with interpretation guided by other oceanographic or meteorological data (Figures C.1 and C.2).

Figure C.1 Time series of several parameters during the first trial deployment in 2015.

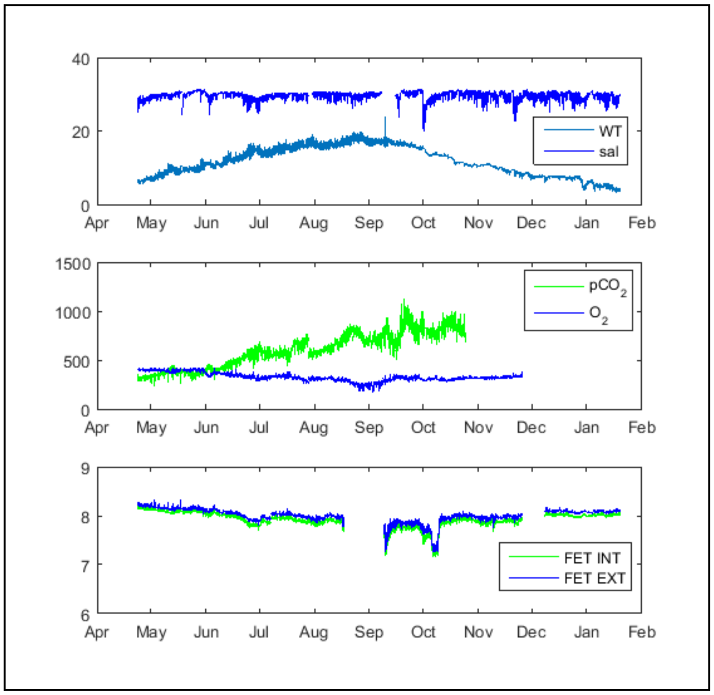
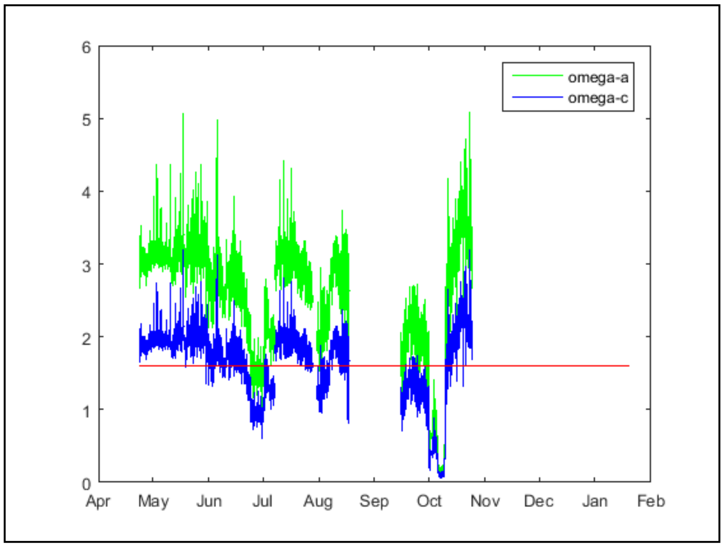


Figure C.2 Calculated omega based on in situ instrumentation during the first trial deployment in 2015.



D. DATA VALIDATION AND USABILITY

D1 Data Review, Verification and Validation

The *in situ* instrument sensors used in this project are factory calibrated or re-calibrated on an annual basis by their respective manufacturers.

All data obtained from *in situ* instrument sensors which are supported by appropriate quality control data and meet the measurement performance specification defined for this project will be considered acceptable and used in the project.

D2 Data Validation and Verification Methods

Quality control of data has been described above, but additional checks of the final data file will be performed before delivery to CBEP. These include checks for:

- Date and time correctly matching up with sensor data;
- Completeness of the data for the period of record;
- Appropriate number of data fields matching the number of sensors deployed and measurements recorded or derived; and
- Missing sequential data value, or gaps in data sequence are explainable (i.e. during data download, sensor malfunction, etc.).

D3 Reconciliation with User Requirements

Upon delivery of the data on an annual basis, the PI will consult with CBEP and EPA project managers to compare data results to the QAPP and to the contract requirements.

E. REFERENCES

Dickson, A.G., J.D. Afghan, and G.C. Anderson. 2003. Reference materials for oceanic CO2 analysis: a method for the certification of total alkalinity. Marine Chemistry 80: 185–197.

Gledhill *et al.*, 2015. Ocean and coastal acidification off New England and Nova Scotia. Oceanography 28(2):182–197, http://dx.doi.org/10.5670/oceanog.2015.41.

Lewis, E., and D. Wallace. 1998. Program Developed for CO2 System Calculations: ORNL/CDIAC-105.

F. APPENDICES

Appendix A: Instrument Operating Manuals and Specification Datasheets (available on request)

SeaFET pH SENSOR USER'S MANUAL
SeaFET Firmware Version 3.6.0 and later
SeaFETCom Software Version 1.2.4
Document No: LP, 3481 North Marginal Road, Halifax, Nova Scotia B3K 5X8 Canada All rights reserved
SAT-DN-00590-1.2.4-51
Date: 2015-01-08 03:36
Available at: http://satlantic.com/seafet
File name: SeaFET-1.2.4-Manual_0_0.pdf
Datasheet available at:
http://satlantic.com/sites/default/files/documents/2015_datasheet_seafet_0.pdf

AFT/SAMI2-CO2 OPERATING MANUAL
Sunburst Sensors, LLC
1226 West Broadway
Missoula, MT 59802
Available at: http://www.sunburstsensors.com/products/oceanographic-carbon-dioxide-sensor.html
File name: CO2 MANUAL SAMI & AFT combined 070912.pdf
Data sheet available at:
The SAMI-CO2 Sensor was independently evaluated by the Alliance for Coastal Technologies and results are reported here:
http://www.act-us.info/Download/Evaluations/pCO2/Sunburst_Sensors_SAMI_CO2/
File name: act_ds10-04_sunburst_pco2.pdf

TD 269 OPERATING MANUAL OXYGEN OPTODE 4330, 4831, 4835 August 2012
Aanderaa Data Instruments AS
PO Box 34, Slatthaug
5851 Bergen, Norway
Available at: http://www.aanderaa.com/productsdetail.php?Oxygen-Optodes-2
File name: Manual Oxygen Optode 4330, 4835 and 4831.pdf
Datasheet available at: http://www.aanderaa.com/media/pdfs/Oxygen-Optode-4835.pdf

SBE-37-SM MicroCat Conductivity and Temperature Recorder Configuration and Calibration Manual
Sea-Bird Electronics, Inc.

1808 136th Place NE
Bellevue, Washington 98005 USA
Available at: http://www.seabird.com/sbe37si-microcat-ctd
File name: SBE_37_manual.pdf
Datasheet available at: http://www.seabird.com/sites/default/files/documents/37-SIbrochureNov14.pdf

Appendix B: Casco Bay Data Processing Steps (in Matlab)

By Chris Hunt, July 2016

1. Assemble all sensor data
    a. combine_SAMICO2.m-reads in each SAMI-CO2 text file, writes out one .mat file with date, time, temperature, CO2, voltage
    b. combine_SAMIO2.m- reads in each Aanderaa Oxygen Optode file (logged by the SAMI-CO2 sensor), converts oxygen voltage, writes out one .mat file with date, time, oxygen
    c. combine_SBE37.m- reads in each SBE-37 data file, writes out one .mat file with date, time, temperature, conductivity, salinity
    d. combine_SeaFET.m- reads in each processed SeaFET data file, writes out one .mat file with date, time, pHINT, pHEXT, and temperature.
2. Combine all sensor data
    a. make_CascoBay_hourly.m:
        i. sets up empty yearly data matrix on hourly time step
        ii. loads SAMI-CO2, oxygen, SBE37, and SeaFET .mat data files
        iii. For each hour of the year, searches for data with matching date and time. Calculates statistics for each parameter for each hour: mean, median, minimum, maximum, standard deviation.
        iv. Writes out hourly Excel data file (i.e. CascoBay_Deployment1.xls)
    b. make_CascoBay_lvl2.m:
        i. reads in Excel file
        ii. adds in empty flag columns for each measurement
        iii. reads in flag file for the appropriate deployment:
            1. Flag 1=All measurements bad
            2. Flag 2=Questionable temperature
            3. Flag 3=Questionable salinity
            4. Flag 6=Questionable SAMI CO2
            5. Flag 9=Questionable FET pH
        iv. Writes out a Level 2 Matlab file, which includes flags (i.e. CascoBay_lvl2_Deployment1.mat)
    c. Make_CascoBay_lvl3.m:
        i. Reads in Level 2 file

ii. Removes any data flagged as questionable in Level 2 file
iii. Calculates omega, TA, and DIC values (from measured CO2 and pH) using CO2SYS software, adds these to data matrix
iv. Writes out a Level 3 Excel file (i.e. CascoBay_lvl3_Deployment1.xls)

Appendix C: UNH OPAL Water Sampling Protocol for TA and DIC

By Chris Hunt, UNH Ocean Processes Analysis Laboratory

Note: If a Niskin bottle is being used, and no Winkler oxygen samples are being collected, the TA sample should be the first withdrawn from the bottle. This ensures a minimal amount of air-water gas exchange, which can shift DIC values:

a. From a Niskin bottle, ensure that the white knob near the top of the bottle is completely shut, and then push in the stopcock near the bottom of the bottle. Very little water should come out of the stopcock.
b. Make sure the bottle is already labeled, as this is hard to do when the sticker is wet. **PLEASE LABEL THE SAMPLE WITH "Casco Bay", THE DATE, THE TIME, AND THE DEPTH.**
c. Dump the DDW from the sample bottle.
d. Rinse the bottle three times with a small amount of water from the Niskin, using the white knob near the top to start and stop flow from the stopcock.
e. Fill the bottle slowly, letting the water run down the side of the bottle. The goal is to prevent bubbles from forming in the sample. Alternatively, and short piece of tubing can be attached to the stopcock and used to fill the bottle from the bottom. Fill the bottle until a very small headspace (bubble) will remain with the stopper in (less than 1% headspace). Flush out the tubing first, squeezing it if necessary to ensure there is no air in the tubing before filling the TA bottle.
f. Stopper the bottle and clamp the positive closure cap over the stopper.
g. When ready, open the bottle again and poison the sample with the Mercuric Chloride solution. For the 60 mL BOD bottles, we use **1 drop** of poison. For the 120 mL bottles we use 2 drops of poison. **Be sure to wear gloves when you do this!**
h. Re-cap the bottle, replace the positive closure, and put into the cooler or other cool dark place for transport back to the lab.
i. Just remember, the whole goal is to get a **bubble-free** sample in the bottle, with a very small headspace under the stopper.

Appendix D: UNH Total Alkalinity Analysis Method for Apollo SciTech AS-A2

By Chris Hunt, version 2, revised Jan 3, 2010

1. Sampling. Refer to the document entitled “UNH Alkalinity Sampling Method”
2. Setup. This procedure is written for the Apollo SciTech AS-A2. This instrument was built by Wei-Jun Cai <wcai@uga.edu> and Yongchen Wang <yongchenw@gmail.com> at the University of Georgia. It performs a Gran titration using dilute hydrochloric acid and a pH electrode, an Orion 3Star. The TA analyzer is operated via a PC computer running Windows.
    a. Here are materials needed during analysis:
        - TA samples, in thermally controlled water bath (24.4 C)
        - Dickson standard, also in water bath
        - 0.1N HCl. We are using premade acid from Fisher
        - 3 pH buffers- usually at pHs of 4.01, 7.00 and 10.01
        - Kimwipes
        - Analysis bottles, glass
        - Magnetic stir bars
        - Tweezers
        - Squirt bottle filled with DDW
        - Logbook
        - Data spreadsheet on a laptop
        - Waste bottle with proper label
3. Starting the machine
    a. Turn on the main power switch on the Apollo Analyzer, and push the power button on the control unit for the pH probe. Boot up the computer, and start the TA program on the Desktop.
    b. The program will ask you if you want to switch the COM ports. Generally you won’t need to.
    c. Put the acid intake tube into the 0.1N HCl, and put the sample intake tube into a beaker of DDW. The machine will then flush out the acid burette.
    d. The software will then bring you to a prompt, instructing you to calibrate the pH electrode. This is generally a good idea, but if you want to skip it, the software remembers the values of the previous calibration.
    e. If the pH electrode is capped, gently remove the cap, unwinding any Parafilm that may be wrapped around it. Also make sure the filler hole near the top of the electrode is unplugged. If the liquid level inside the electrode is more than a centimeter or two below the filler hold, add some of the electrode filling solution.
    f. Rinse the outside of the pH electrode with DDW. This is one of the most sensitive steps in the analysis, and needs to be done carefully every time. Generally, you want to minimize the amount that the electrode is contacted. Here is the technique:

    - Rinse the electrode from the bottom of the Parafilm wrap to the tip of the bulb. Use your rinse beaker to catch the last drop from the bottom of the probe, but be careful not to touch the beaker to the probe itself.
    - Fold a Kimwipe three times, so it is long and skinny. Wrap this around the electrode, from the narrow part above the bulb upwards. Reverse the Kimwipe and repeat.
    - Then, take the edge of your folded Kimwipe and VERY carefully daub up any remaining drops of water left. Be sure to check the narrow band above the bulb- water can hide in there.
    - Your electrode is ready to go!

4. pH electrode calibration
    a. If you want to calibrate the pH electrode, the software asks you for the pH value of the first buffer, followed by the EMF reading. Enter the pH buffer value, then dip the electrode into the pH solution. **The bulb of the electrode, as well as the little white dot on the side of the electrode just above the bulb (the reference junction), must both be a least 1mm below the surface of the solution.** You don't need to stir the pH buffer.
    b. Wait until the EMF reading on the pH electrode control unit is very stable, i.e. not changing for 8 seconds. Be patient, this is important.
    c. Enter the EMF reading into the software, then repeat for the other two pH buffers.
5. Calibrating the acid
    a. At this point, the software will ask you to enter the concentration of the acid. The concentration is very close to 0.1N; however, it is NOT exactly 0.1N. Calibration of the acid takes this discrepancy into account, as well as any subtle, funky behavior of the electrode. Calibrating the acid is VERY important whenever using a different bottle of acid or a different pH electrode.
    b. The software will then prompt you to enter the concentration of the standard. In this case, the standard is the Dickson standard, which the machine will use to back-titrate the acid. The key thing to get correct here is the units: the machine wants the Dickson standard in **mmol/L**, not the umol/kg that Dickson reports it in. Converting the Dickson concentration to mmol/L is temperature dependent, there should be a spreadsheet in the lab giving the Dickson concentration at whatever is the temperature in the lab. Enter this number!
    c. The machine will then perform a series of titrations of the Dickson standard, and report the concentration of the acid (which also takes into account abnormal electrode behavior). Usually after three titrations the machine arrives at a stable reading, and takes that value as the acid concentration. Be sure to enter this number in the logbook!
6. Dickson check
    a. At the beginning of each day, we need to make sure the machine is working satisfactorily. We use the Dickson standard to do this: by running this standard as a sample and comparing the results against the known concentration, we can assess the machine's performance. Usually you'll have to run the standard three times in the

morning: the first value is almost always bad, and you want to get at least two readings that are within 10 umol/kg of the standard value before proceeding to samples. You want to run standards until they are within +/- 2 umol/L of each other. There may be an **offset** from the true value of the Dickson standard, but this can be subtracted- the important part is to get the precision to an acceptable level.

b. When running any sample, including the standard, the software gives you three options on the screen:
    - 1. Calibrate pH electrode
    - 2. Known salinity sample
    - 3. Unknown salinity sample

c. The salinity of the Dickson standard is known, so pick Option 2 and enter that value if you're running the standard. We pull salinity matchups of many other samples, so if the salinity is known choose Option 2. There should be a printout of these salinities with the logbook. If the salinity is unknown, choose Option 3.

7. Running a sample
    a. The software is pretty good at prompting you step-by-step throughout the analysis process. First, take the electrode out of the previous samples, and remove and rinse the stir bar. Put the stir bar onto some Kimwipes to dry. Place a dry stir bar into a new sample cup. Hold a waste beaker under the electrode, and rinse the electrode body with DDW. Wipe the electrode as detailed above. Put the new sample cup under the electrode, and lower the pH probe to the stop point.
    b. Gently invert your sample upside-down a couple times to mix, then remove the stopper. Place the sample tube into your sample bottle, the outlet for the sample pipette into the sample tube rinsing syringe, and hit Enter on the keyboard. The machine will then rinse the sample pipette a couple times- with the rinse water draining into a waste bottle below- then withdraw your sample volume (typically 20 mL). When this is complete, CAREFULLY and SLOWLY move the outlet tube to your sample cup, and hit Enter again on the keyboard. The machine will begin to dispense the sample. **CAREFUL!** Sometimes the force of the sample being dispensed will fling the sample tube out of the sample cup- you probably want to hold the sample tube while the machine is dispensing. Also, make sure you don't splash sample onto the sides of the sample cup- this will produce bogus TA values.
    c. When the sample has been dispensed, CAREFULLY and SLOWLY remove the outlet tube and put it in a waste container. Don't drag the sample tube along the sides of the sample cup.
    d. Turn on the stir bar so it is turning fast but not splashing the sample around, and hit Enter on the keyboard. This will begin the titration. At this point you just need to wait. The machine will wait until it reads a stable initial pH, then inject a dose of acid, re-read the pH, then add small doses of acid and measure the slope of the pH curve with each acid addition.

   e. When the analysis is complete, the computer will beep. Record the volume of acid, TA, and time in the lab notebook, and on the TA spreadsheet as well. It is very important to keep the TA spreadsheet up-to-date!
   f. If you are running a Dickson standard, enter the data in the 'Standards' tab of the Excel file. **You need to do this in order to determine how the machine is performing!** The spreadsheet performs several calculations, without which you cannot compare the analysis result with the standard value.
   g. Throughout the course of a day of instrument operation it is important to check the Dickson standard, to make sure the instrument is still performing well. Usually, running one analysis of the Dickson standard every 5 samples is sufficient.
   h. Also, at the end of the day be sure the run the Dickson standard one last time. It is important to have a good measurement of the Dickson standard at the beginning and end of each day, to ensure good data for that day.
8. Shutting down
   a. When you've run the final Dickson standard for the day, choose 'End' in the software. It will prompt you to put both sample and acid tubes into DDW, and then it will flush both pipettes. If you'll be running more samples soon, you can leave the probe in the last sample and turn the stir bar off. If the machine will be idle for more than a couple days, place the pH probe in some old pH 4 buffer. Plug the filler hole in the electrode, and you're done! Go home!

Appendix E: DIC Analysis Method for Li-Cor LI-6262

By Chris Hunt, revised March 9, 2011

1. Turn on the Main Power switch, followed by the power switch on the Li-Cor LI-6262.
2. Make sure the bottom line of the Licor display reads Int. If not:
   a. On Licor, hit Function button, then 09, then enter. Set Channel to 22, Start to Thrsh, Thrsh=1.0, End-Thrsh.
   b. Hit Function, then 04. Set bottom line to Channel 46.
3. Turn on N2 gas flow (first main valve on top, then small black valve on regulator)
4. Flush syringe twice with Dickson standard, holding syringe upright to flush any air out, then fill halfway.
5. On computer, double-click "DIC62final.exe" icon on desktop.
6. Run Dickson standard: 0.75 mL, 0.5 mL, 0.25 mL and 0.01 mL. Run each volume multiple times until consistent value is repeated. Always read Int value from Licor, ignore the Peak Area on the computer. Record time and temperature each time.
7. Flip each sample upside-down several times to mix before running.
8. Run samples (1.0 mL), recording time and temperature of each analysis.
9. Please enter data both in the logbook and computer spreadsheet.

10. Remember to check the Dickson standard every 5 samples. If it does not agree, we need to figure out why.
11. Also remember to run a Dickson standard at the very end of the day.
12. Before shutting down, run 1.5 mL of DDW as a sample to flush
13. To shut down, turn off N2 gas first (both valves), LI-6262, and the Main Power switch last.
14. Turn off computer.

DIC Method Notes

Analysis Notes:

1. It is very helpful to sort samples by salinity, and run them in groups of similar salinities.
2. The nominal volumes of standards needed to prepare the calibration curve are: 0.05 mL, 0.25 mL, 0.50 mL, and 0.75mL. 4-5 runs are needed for the first value while only 3 are needed for the rest.
3. A standard check should be performed at least twice a day: once in the middle of the run, and once at the end. The volume of the standard check should be .50 mL, and the standard should be run at least 3-4 times for each check.
4. The recipe for the acid is: 450 mL DDW, 50 mL Phosphoric Acid, and 50 g NaCl.

Data Entry Notes:

1. The file for DIC data is called DIC_master_lvl1.xls
2. Data from the beginning of the day, used to determine the standard curve, should be entered in the “standard_curve_data’ worksheet.
3. Data from unknown samples should be entered in the ‘sample_data’ worksheet.
4. Data from the standard checks in the middle and end of the day should be entered in the ‘standard_checks’ worksheet.
5. Column U of the ‘sample_data’ worksheet and column P of the ‘standard_checks’ worksheet should be filled with -9999, to prepare for the DIC processing code.
6. Dates of DIC runs need to be entered into the ‘DIC_dates.xls’ file.