

Shell Day

Quality Assurance Project Plan

RFA #19110

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Prepared by Shell Day Science Advisory Team



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This QAPP was written using the templates (or sections) from the Handbook for Citizen Science Quality Assurance and Documentation published in 2019 and available here: <https://www.epa.gov/citizen-science/quality-assurance-handbook-and-guidance-documents-citizen-science-projects>. The sections in this QAPP, however, have been re-organized and are not in the same order of the templates in the handbook.

1. Problem Definition, Background and Project Description

A. Problem Definition

The coastal and nearshore environment, while representing only a marginal area of the total ocean, is valuable economically and culturally. Coastal ecosystems are exposed to the changes brought on by ocean acidification in general, but also display notable differences in their biogeochemical features. The Northeast United States and the Gulf of Maine are especially vulnerable to ocean and coastal acidification (OCA) due to relatively colder temperatures inducing naturally lower calcium carbonate saturation, relatively lower buffering capacity of riverine inputs, and an outsized dependence of the marine resource economy on shell-forming organisms.

It is particularly important to understand the ability of marine environments to resist acidification or “buffer” increases in hydrogen ion concentration (corresponding to a decrease on the pH scale). The buffering capacity of a coastal ecosystem can be described by the total alkalinity – a key parameter of the carbonate chemistry of coastal and oceanic waters. But total alkalinity measurements are either too expensive or unavailable to most community water monitoring organizations. In oceanic waters, total alkalinity can often be related to salinity, but this relationship is not well established in coastal waters. The Shell Day project aims to investigate the relationship between salinity and total alkalinity among individual estuaries and embayments using a distributed community sampling approach. If salinity can be developed as a proxy for total alkalinity, we may be able to use widely available coastal salinity measurements to help characterize local coastal areas that are more vulnerable or resilient to acidification.

B. Background

Ocean acidification is a process by which increasing anthropogenic CO₂ in the atmosphere is absorbed at the ocean surface, thereby acidifying marine waters and lowering pH. Lower pH affects calcium carbonate by reducing the saturation state of calcium carbonate, referred to as omega (Ω), a gradient across which calcium carbonate is either readily available to organisms (high Ω / high saturation state), or is more difficult to extract from the water column or even prone to dissolving the shells of living creatures (low omega / low saturation state). The open ocean surface has changed on average to become 30% more acidic than baselines before the rise of CO₂-intensive industry (Orr et al. 2005). Future projections for acidification anticipate an ocean with steep declines in the populations and home-ranges of calcifying organisms — and hypothesize substantial changes in food web complexity and dynamics. These changes accompany a suite of stressors on marine ecosystem functioning, the health and abundance of commercial and ecologically important species and the provision of ecosystem services at large.

In the Northeast, additional nearshore drivers can substantially exacerbate the severity of acidification (Wallace *et al.* 2014, Gledhill *et al.* 2015). Northeast rivers are lower in buffering capacity, as measured by total alkalinity from river inputs, making storm water inputs naturally acidic. The Northeast also suffers from nutrient enrichment which leads to algal blooms; the biological decay of these blooms delivers additional CO₂ to bottom waters, causing localized acidification events. Also, changes to habitat and predation from the invasive green

crab have reduced wild populations of many shellfish, thus limiting the robustness of shellfish populations now coping with acidification processes.

While mitigation of the global rise in atmospheric CO₂ relies upon large-scale systemic changes for energy and resource use, some of the nearshore dynamics of the local stressors that exacerbate coastal acidification conditions are within the control of place-based management. To mitigate the impacts of coastal acidification, and evaluate interventions for resilience, it is necessary to monitor conditions at high geographic and temporal frequency. In the Northeast, there are routine monitoring programs (including research programs), and several continuous monitoring stations for carbonate parameters. This project will better characterize ocean and coastal acidification in a spatial- or regional- context, utilizing the work and experience of existing networks of community water quality monitoring organizations.

In 2018, EPA published “Guidelines for Measuring Changes in Seawater pH and Associated Carbonate Chemistry in Coastal Environments of the Eastern United States” (Gear and Pimenta 2018). The Northeast Coastal Acidification Network (NECAN) supplemented these guidelines with a series of on-line and hands-on workshop trainings in Connecticut, Massachusetts, and Maine. NECAN staff and partners met with stakeholder groups and more than 40 community water monitoring programs in 2018 to focus on approaches for monitoring acidification directly and understanding related nearshore processes. A survey of community water quality organizations showed capacity for building in OCA monitoring into existing organizations activities. These guidelines from EPA have been used to inform the sampling protocol and trainings associated with Shell Day.

C. Project Description

Shell Day seeks to engage the network of community water monitoring organizations involved in the 2018 trainings to participate in a distributed and simultaneous coastal acidification monitoring event. During the August 2019 single day sampling blitz, monitoring organizations across the Northeast will measure their routine series of water quality parameters, and collect water for analysis of total alkalinity. The project team (see Section 2) will provide bottles, field datasheets, and training to these organizations. The project team will then bring the bottles to partnering EPA and university laboratories. Data will be analyzed to evaluate the relationship between salinity and total alkalinity among individual estuaries and embayments, as well as potentially for regional relationships among groups of estuaries or embayments.

Shell Day Project Objectives are:

1. Leverage a distribution of community water monitoring organizations to conduct a one-day regional monitoring program, identify and compare alkalinity distributions among estuaries, and test whether salinity can be a proxy for total alkalinity in coastal waters.
2. Motivate community water monitoring organizations to participate in coastal acidification research and to access and use state and federal research and information resources and learn about the role of coastal drivers in coastal acidification.

Project Outputs (linking data results to actions)

1. Snapshot of total alkalinity (TA) and saturation state where pH measurements are available
2. Spatial distribution of TA and pH on regional and sub-regional (*e.g.*, Gulf of Maine, southern New England, Long Island Sound) basis
3. Relationship between TA and salinity on a regional and sub-regional basis
4. Pilot study to test approach of using community water monitoring organizations
5. Evaluate the potential for this network to interface with ongoing monitoring for acidification including future EPA National Coastal Conditions Assessments.

The project is funded partially by a grant to NERACOOS from the NOAA Ocean Acidification Program. The funds will be used to reimburse partnering university laboratories. In addition, small grants from the American Geophysical Union to MIT Sea Grant will be distributed to community water monitoring organizations to assist with sample collection and transport as needed.

Data collection approach

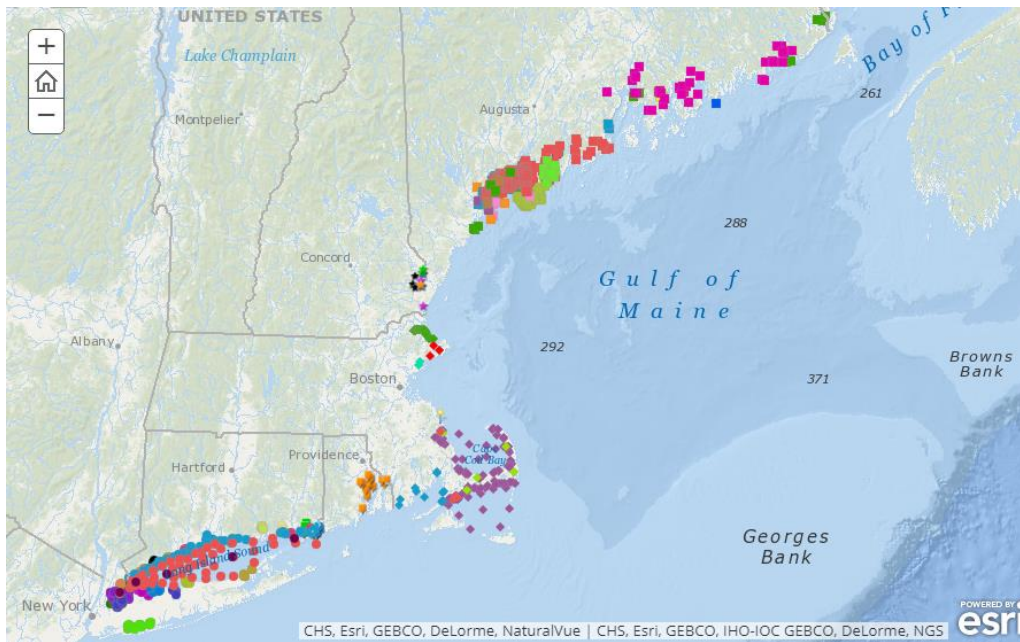
The primary data being collected are total alkalinity, salinity and water temperature. For each site, we are asking organizations to document the tidal stage, water depth and coordinates. Ancillary data will be specific to each organizations' instrumentation and may include pH, Secchi disk depth, nutrient measurements, colored dissolved organic matter (CDOM), dissolved inorganic carbon (DIC), light attenuation, chlorophyll *a*, oxygen concentration and other measurements.

Surface water samples will be collected at about 0.5 meters depth from a dock, pier, shore, or boat. Samples will typically be collected using a bucket and poured into a pre-labelled 120 mL HDPE (high density polyethylene; plastic) wide mouth bottles.

See Section 8 for additional information.

Geographic range

The geographic range of the project is shown below. This graphic includes known monitoring stations from ~60 monitoring programs surveyed in 2018. The color coding indicates different groupings of organizations with potential partnering laboratories and is not significant.



Time period

August 22 is Shell Day. It is selected because a low tide and high tide in the morning and afternoon is at a reasonable time for sampling by volunteers. Two duplicate samples will be collected in the morning at low tide, one sample at mid tide, and two more duplicate samples will be collected in the afternoon at high tide.

We are asking organizations to select sites that focus on the greatest salinity gradient (difference between salinity at high and low tides). Other considerations for site selection include: practicality and accessibility of sampling location, and the presence of wild or aquacultured shellfish that may be affected by acidification processes.

We are asking organizations to measure temperature and salinity *in situ* using the same water sample, using methods previously documented by the organizations, such as a multi-meter probe, a refractometer, or a hand-held thermometer.

After sample collection, bottles will be kept on ice and on August 23 samples will be transported or shipped to regional collection locations and partnering laboratories for analysis or preservation for later analysis.

Also, on August 23 some science advisors will operate on-site TA measurement instrumentation near the collection locations and continue conversations about coastal acidification via a laboratory open house and celebration for Shell Day participants.

Data Users

Data synthesis will be led by NECAN research partners and participating organizations (Section 2).

Results will be formulated into usable figures, tables, data files, maps, or other products.

We will schedule webinars to discuss and share results in the fall of 2019 and winter of 2019-2020.

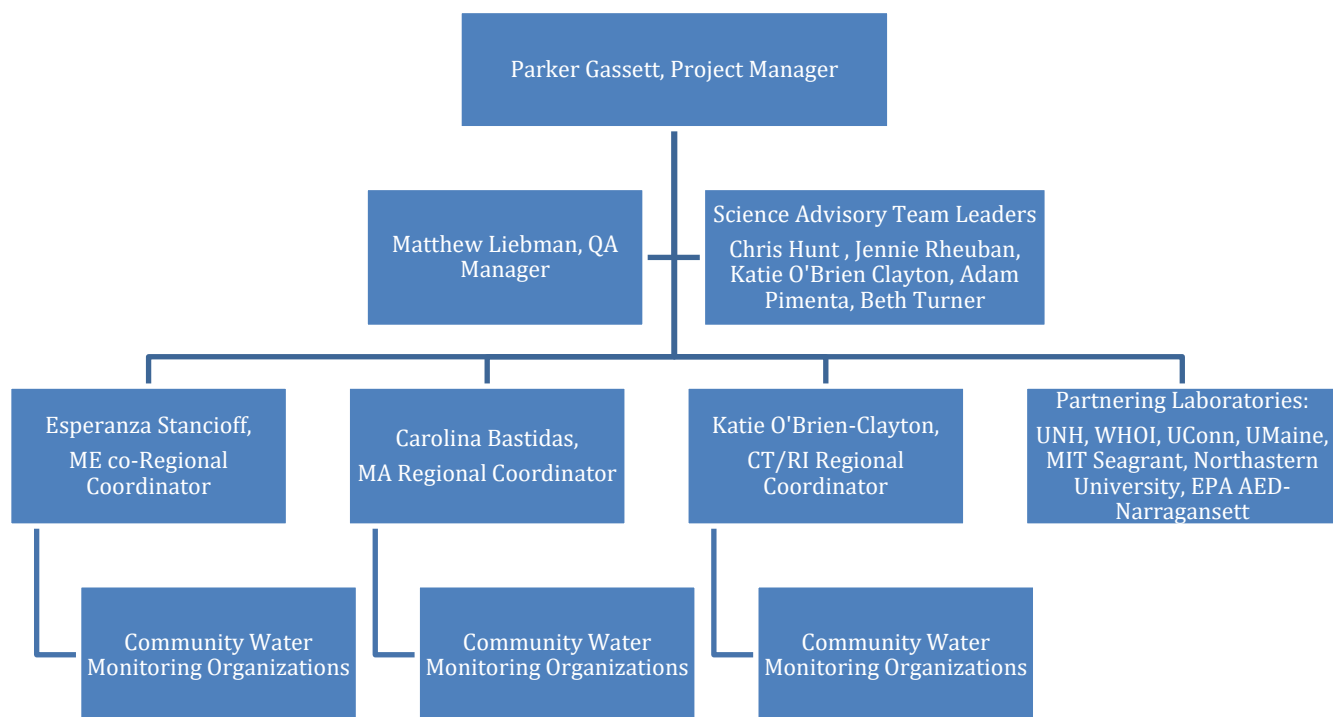
Data users also will include coastal managers and scientists, water quality monitoring organizations, environmental chemists involved as partners in the project, science outreach professionals and funding agencies (e.g. NOAA OAP and EPA).

Participants will be from water monitoring organizations listed in **Attachment 1**. Following Shell Day, a complete list of participants will be confirmed.

2. Project Organization, Chart and Distribution List

Name	Title	Organizational Affiliation	Responsibilities
Parker Gassett	Project Manager	University of Maine (UMaine)	Coordinator for all moving parts and coordinator with Maine monitoring organizations
Esperanza Stancioff	Regional Coordinator	University of Maine (UMaine)	Secondary coordinator for Maine monitoring groups
Carolina Bastidas	Regional Coordinator	Massachusetts Institute of Technology (MIT) Sea Grant	Regional head for Mass., primary liaison to Massachusetts monitoring groups
Katie O'Brien Clayton	Regional Coordinator	CT Department of Energy and Environmental Protection (DEEP)	Regional head for LIS, primary liaison to Connecticut/Rhode Island monitoring groups, lead scientist in generating the field datasheet
Emily Silva	NECAN Coordinator	NERACOOS (Northeast Regional Association of Coastal Ocean Observing Systems)	Assist with project coordination, training webinars, perform data entry
Chris Hunt	Principal Investigator, Laboratory Manager and Science Advisory Team lead	University of New Hampshire (UNH)	Regional lab support for NH and ME, Principal Investigator leading and coordinating data interpretation
Jennie Rheuban/Dan McCorkle	Laboratory Manager and Science Advisory Team lead	Woods Hole Oceanographic Institution (WHOI)	Regional lab support, co-coordination for Massachusetts, lead for training videos and webinars
Adam Pimenta/Jason Gear	Laboratory Manager and Science Advisory Team lead	EPA Atlantic Ecology Division (AED)- Narragansett Laboratory	Regional lab support for Rhode Island
Matthew Liebman	Quality Assurance Manager and Science Advisory Team	EPA Region 1	Logistics support for MA and QA Manager, audits community water monitoring organizations
Beth Turner	NOAA Agency Representative	NOAA National Ocean Service	Science Advisory Team representative, logistics support
Kate Liberti	Laboratory Manager	UMaine Darling Marine Center	Regional lab support for ME

Michele Lavigne	Laboratory Manager	Bowdoin College	Regional lab support for ME
Isaac Westfield	Laboratory Manager	Northeastern University Marine Science Center	Regional lab support for MA
Ryan Woosley	Laboratory Manager	MIT	Regional lab support for MA
Penny Vlahos	Laboratory Manager	UConn	Regional lab support for LIS
Community water monitoring organizations	Field sampling	See Attachment 1 for list	Participate in training, sampling and outreach



The QAPP will be distributed to the Regional coordinators and the Laboratory Managers. Some of the community water monitoring organizations may request a QAPP. The monitoring organizations will get the sampling protocol and be trained by video.

3. Data Quality Objectives and Indicators

A. Data Quality Objective

Data quality objective: Use naturally occurring tidal variability to test whether salinity provides a statistically significant predictor of total alkalinity regionally or locally during a single tidal cycle.

B. Data Quality Indicators

The table below provides data quality indicators for field collection of water samples, preservation, storage, and laboratory analyses of **total alkalinity** only.

Data quality indicators	Quality control activities and checks	DQI goals
Precision	Field and laboratory replicates. We will collect duplicates for morning and afternoon samples only. They will be considered field duplicates. Partnering laboratories will perform duplicates on 10 percent of samples. Some laboratories perform 2 to 4 laboratory replicates for each sample.	1 percent RPD (relative percent deviation) or RSD (relative standard deviation) for field duplicates. For lab replicates, 0.4 to 0.5% RPD. If too high, samples are re-run.
Bias	Compare certified reference materials (CRMs) pre-and post-calibration daily batches	Data are not biased in a particular direction, and correction factor applied if necessary. Note that blanks (e.g. use of DIW) are typically not used for measures of total alkalinity because it is unclear where a source of contamination would be from.
Accuracy	Calibrate instrument to CRMs. All laboratories will use CRMs from the same source (Andrew Dickson, UCSD).	Calibrations within acceptable limits (or acceptance criteria): $< \pm 10 \mu\text{mol/kg}$ May apply a correction factor based on pre and post calibration.
Representativeness	Evaluate whether sample distribution was sufficient to characterize an individual system or larger regional system	Data collected represent the individual or regional system and are not biased. We will ask: -Will the data collected inform our ability to estimate alkalinity in coastal sites or in a larger region? -Are data measured representative of conditions at a particular collection site on the specific day of collection? -Can data inform understanding of the potential range of alkalinity variability and alkalinity sources in a region?

		-Compare number of watersheds sampled to total potential watersheds Note that representativeness is determined by participation from groups
Comparability	Compare results to studies previously or concurrently conducted in these regions or by these institutions: <ul style="list-style-type: none"> University of Maine Darling Marine Center in mid-coast Maine University of New Hampshire in the Gulf of Maine Woods Hole Oceanographic Institution in Buzzards Bay EPA AED-Narragansett Laboratory for Narragansett Bay Stony Brook University in Long Island Sound University of Connecticut in Long Island Sound Massachusetts Institute for Technology 	Data collected are sufficiently similar in methodology to permit a meaningful analysis. Results from this study fall within the range documented in other efforts.
Completeness	Compare to intended sampling goals to meet the project purpose	Measures of completeness: Incomplete=one sample at a site, or a system Partially complete=two or three sampling conditions (low, mid, or high) Complete= three sampling conditions (low, mid, high) 50% participation of identified groups 3 to 5 groups participate from each region (LIS, Mass, GOM)
Sensitivity		Titration that measure total alkalinity do not report a detection or reporting limit, because TA is so abundant.
Measurement range	Evaluate maximum and minimum values	Expected range of total alkalinity is about 1000 to 2000 $\mu\text{mol/kg}$ at the range of salinities expected, from 10 to 32 ppt (psu)

For measures of *salinity*, we will have limited control on methods and quality control of community water monitoring organizations but will require documentation of a Quality Assurance Project Plan or equivalent. We are asking each organization to provide information on whether they have a QAPP in place, and when the meters were last calibrated. Many organizations have QAPPs in place, including those under the umbrella of

Rhode Island Watershed Watch, Long Island Sound Unified Water Study, Buzzards Bay Coalition, Massachusetts Bays Program, Salem Sound Coastwatch, Piscataqua River Estuaries Partnership, Friends of Casco Bay, and the Maine Coastal Ocean Alliance. Many organizations will be using hand-held multimeters or refractometers. Based on a review of these meters, instrument accuracy (or uncertainty) is typically 0.1 practical salinity units (psu, or parts per thousand; or 1% of the reading) and resolution (or sensitivity) is 0.01 psu. For refractometers, accuracy is 0.2% with a resolution of about 0.2 salinity units. An error of 0.1 psu equates to about 5 μmol per kg of total alkalinity, which is within our performance goal of 10 μmol per kg.

4. Project Schedule

Activities	Group/Person responsible for activity completion	Timeframe work will be done
Recruit regional coordinators and Science Advisory Team	Gassett, Stancioff	March to April 2019
QAPP developed	Science Advisory Team	May to July 2019 Biweekly calls
Recruit organizations Outreach to community water monitoring organizations via phone/email/mailed flyers (June)	Regional coordinators – Gassett, Stancioff, Bastidas, O'Brien, Rheuban	May to July Biweekly calls
Develop and provide 2 training materials as webinars	Science Advisory Team	July to August 2019
QAPP approved	EPA	August 2019
Monitoring groups select stations with regional coordinators	Regional coordinators	August 2019
Share educational materials with community organizations	Regional coordinators and Science Advisory Team	August 2019
Final logistics planning Ship bottle and sampling supplies, datasheets and waterproof bag (sampling kit) to participants	Regional coordinators and Science Advisory Team	Early to mid-August 2019

Shell Day	Regional coordinators and Science Advisory Team	August 22 to 23, 2019
Analyze samples	Regional labs	August to September, 2019
One-month post survey participants	Regional coordinators	September, 2019
Interview key project personnel	Parker Gassett	September, 2019
Results webinar and sharing of usable materials	Regional coordinators and Science Advisory Team	November to December, 2019
Report to NOAA Ocean Acidification Program	Regional coordinators and Science Advisory Team	July 2020
12-month post-survey of participants	Regional coordinators and Science Advisory Team	July 2020

5. Training and Specialized Experience

A. Training

Personnel/Group to be Trained	Description of Training (Including Trainer(s))	Frequency of Training
Monitoring groups	<p>Sample collection and preservation, measurement of temperature. Training via video, webinar and written materials</p> <p>Webinar reviewing sampling protocol, datasheet details, and primary hypotheses for the project</p> <p>Training video: filmed and edited by WHOI Sea Grant (Jennie Rheuban)</p>	Once, one month before Shell Day

B. Specialized Experience

Person	Specialized Experience	Years of Experience
Chris Hunt, UNH	Laboratory analyses for total alkalinity and other carbonate chemistry parameters	15 years
Kate Liberti, UMaine Darling Marine Center	Laboratory analyses for total alkalinity	6 years, including work at EPA AED-Narragansett Laboratory
Michele Lavigne, Bowdoin College	Laboratory analyses for total alkalinity	5 years
Isaac Westfield, Northeastern University	Laboratory analyses for total alkalinity	10 years
Ryan Woosley, MIT	Laboratory analyses for total alkalinity	12 years
Jennie Rheuban/Dan McCorkle, WHOI	Laboratory analyses for total alkalinity and other carbonate chemistry parameters	5 years (Rheuban) to >10 years (McCorkle)
Jason Grear/Adam Pimenta, EPA AED-Narragansett Laboratory	Laboratory analyses for total alkalinity and other carbonate chemistry parameters	5 to 10 years. There might be a Laboratory Quality Assurance Management Plan in place also.

Penny Vlahos, UConn	Laboratory analyses for total alkalinity and other carbonate chemistry parameters	5 years, including 4 months on Hydros
Parker Gassett, UMaine	Citizen science and community engagement coordinator	4 years

6. Existing Data and Data from Other Sources

A. Existing data

We will compare results to data collected by the following institutions:

- University of Maine Darling Marine Center for mid-coast Maine samples
- University of New Hampshire in the Gulf of Maine
- Woods Hole Oceanographic Institution in Buzzards Bay
- EPA AED-Narragansett Laboratory in Narragansett Bay
- Stony Brook University in Long Island Sound
- University of Connecticut
- Massachusetts Institute For Technology
- University of Rhode Island

Some of these institutions have collected total alkalinity data directly. Others have collected other carbonate parameters that allow us to calculate TA or associated parameters, such as carbonate saturation, or omega.

B. Data sources

The data sources will include peer-reviewed academic journals, continuous monitoring results, government data reports, unpublished data, etc.

C. Data usage

These data will be used to compare with concurrently collected data for TA and salinity relationships, and may be used to evaluate expected ranges of data from studies conducted within the last ten years.

D. Requirements and limitations

We will evaluate quality of the data based on: standardized protocols in place and followed; whether QAPPs or equivalent documents are available, whether metadata are available; and whether QC flags are utilized.

7. Sampling Design and Data Collection Methods

A. Sampling Design

We are collecting all samples during the day on August 22, regardless of weather conditions. This approach aims to generate a regional snapshot of carbonate chemistry conditions, and to acquire a range of tidal and temperature conditions to establish the total alkalinity-salinity relationship.

Samples will be collected from docks, piers, shore, or boats, with buckets lowered into the water.

We plan to collect samples on a day when low tide is generally in the morning in New England. For example, low tide on August 22 in Salem is at 10:25 am EDT, and high tide is at 4:38 pm EDT. We will take two samples at low tide, one sample at mid tide, approximately 1:30 pm EDT, and two samples at high tide. The two samples at low and high tides are field duplicates. Our goal is to collect samples within 30 minutes of the target tidal stages based on comparison to tide tables (e.g NOAA), or local knowledge and observation.

B. Methods

All samples are grab samples. Organizations will provide their own measures of temperature and salinity using hand held multimeter probes, refractometers or handheld thermometers. Although we don't have much control on the quality of these instruments, we are asking each organization to provide information on whether they have a QAPP in place, and when the meters were last calibrated. Many organizations have QAPPs in place, including those under the umbrella of Rhode Island Watershed Watch, Long Island Sound Unified Water Study, Buzzards Bay Coalition, Massachusetts Bays Program, Salem Sound Coastwatch, Piscataqua River Estuaries Partnership, Friends of Casco Bay, and the Maine Coastal Ocean Alliance.

Ancillary field information, including date of last calibration of meters, will be included in a field datasheet (**Attachment 2**; see Section 12).

Here is the Standard Operating Protocol (SOP) for sampling surface water. Sampling from a dock or pier is preferred but wading into water, or sampling by boat, is allowable. Bottles will be pre-labelled.

All sample collection methods, including sampling via a bucket, hand, and pole, are in **Attachment 3** and provided at the Shell Day website (www.necan.org/shellday), and also presented in a video (on a webinar and at the website).

Below is the protocol for the preferred (and most likely the most common) method using a bucket from a dock or pier:

Bucket sampling protocol:

- 1) *If using a multiparameter data sonde, measure temperature and salinity as per your normal measurements (and other parameters) in the water body. Record the data and time on the datasheet.*
- 2) *Fill bucket*
 - *Fill bucket ¼ full to rinse bucket with site water*
 - o *Take care not to stir up any sediments if sampling very shallow sites*
 - o *If wading into your site, take care to fill the bucket upstream of where you are standing*
 - *Swirl water around in bucket to rinse.*
 - *Dump rinse water downstream of where you will be sampling*
 - *Fill bucket with site water, ½ to ¾ full.*
 - *Note the time the water was collected from the field site.*
 - *Set bucket on dock, pier, ground, etc.*
- 3) *If using another method for temperature and salinity, measure temperature and salinity in the bucket. Record the data and time on the datasheet.*
- 4) *Rinse sample bottle*
 - *Keep the cap on the bottle, put sample bottle into bucket until the entire bottle is submerged.*
 - *Open the bottle underwater with the mouth ~10cm from the surface of the bucket.*
 - *Dump out half of the water, put cap on bottle, shake bottle to rinse and dump out water. Do not dump the rinse water back in the bucket.*
 - *Repeat bottle fill and rinse two more times.*
- 5) *Fill sample bottle*
 - *Keep the cap on the bottle, put sample bottle into bucket until the entire bottle is submerged.*
 - *Open the bottle underwater with the mouth ~10cm from the surface of the bucket.*
 - *Dump out a small amount of water to leave a little headspace at the top of the sample bottle.*
 - *Cap bottle, place on ice in a cooler.*
 - *If collecting a duplicate sample, repeat the bottle rinse and fill for the second bottle (#4 and #5).*
- 6) *Fill out the rest of the data on datasheet: be sure to record time of sample collection, bottle numbers, temperature, salinity, tidal stage, and any other ancillary measurements.*

If collecting a sample by hand without a bucket (if you can reach the water by hand), skip #2 and proceed to #3. Try to measure temperature and salinity (and other measurements) as close to the time of bottle collection as possible and at the same depth as where the sample was collected.

If collecting a sample with the sampling pole method, complete #1 and proceed to the sampling pole protocol.

C. Locations

We are sampling at multiple locations in estuaries and coastal waters throughout New England. These locations are listed in the project description. The target salinity range is from 10 to 32 psu (i.e. ppt). The main criteria for site selection include ease of access for sampling, expectation of wide range of salinity due to tidal range.

D. Frequency

We are taking samples on one day, to simulate a “blitz” and acquire a one-day snapshot of regional picture of total alkalinity.

E. Quality control

Samples in morning and afternoon will be duplicates to estimate potential field variability.

Some samples will be co-located with other instruments, such as continuous monitoring stations located in Casco Bay, Great Bay, or Duxbury Bay. These locations are still to be determined.

F. Data Collection Methods summary table

Matrix	Parameter	# of Sampling Locations	# of Samples per Location	Type of Field QC Samples	Total Number of Samples/ Measurements	Sampling SOP Reference (Attach SOP to the QAPP)
Water	Total Alkalinity	Many	5	Duplicates in morning and afternoon samples	300 to 500	Sampling SOP and video available at www.necan.org/shellday
Water	Salinity	Many	3	Depends on organization	300 to 500	Depends on organization QAPP or equivalent documentation
Water	Temperature	Many	3	Depends on organization	300 to 500	Depends on organization QAPP or equivalent documentation

8. Sample Handling and Custody

A. Summary table of activities

Activity	Name/Organization	Contact Information
SAMPLE COLLECTION, PACKAGING, & SHIPMENT		
Sample Collection	Community water monitoring organization	See Attachment 1
Sample Packaging	Community water monitoring organization	See Attachment 1
Coordination of Shipment	Regional coordinators	Regional coordinators
SAMPLE RECEIPT & ANALYSIS		
Sample Receipt	Regional coordinators	See list of regional coordinators
Sample Custody & Storage	Laboratories	See list of laboratory managers
Sample Preparation	Laboratories	See list of laboratory managers
Sample Analysis	Laboratories	See list of laboratory managers
Sample Archiving (if appropriate)		
Sample Disposal (if appropriate)		

B. Sample Identification Procedure

Each sample will have a unique ID, numbered according to region and sampling location or group.

C. Chain-of-Custody Procedures

The field datasheet (**Attachment 2**) will double as a chain-of-custody form. This will be signed by the field sampler, the regional coordinator and the laboratory managers.

D. Field Sample Custody/Tracking Procedures

Samples will be stored on ice in plastic bags with datasheets. Regional coordinators will deliver samples to partnering laboratories on August 23. Laboratories will preserve samples not immediately analyzed using mercuric chloride at .02 to .05% of volume. Maximum holding time for shipment to laboratories is 24 hours.

E. Laboratory Sample Custody/Tracking Procedures

Each lab may have its own tracking system.

9. Analytical Methods

Matrix	Analytical group or parameter	Reporting or Detection Limits	Analytical and Preparation Method/SOP Reference	Sample Volume	Containers	Preservation Requirements	Maximum Holding Time (preparation and analysis)
Water	Total Alkalinity	Not applicable	Potentiometric, see Pimenta and Grear, 2018 Based on Dickson, 2007	120 ml or less	HDPE 120 mL	Saturated mercuric chloride, less than 0.5% of total volume of samples	If preserved with mercury, up to a year; if stored at 4° C, 24 hours (assumed)

Each lab uses a different brand of titrator to measure total alkalinity.

Partnering Laboratory	Titrator Brand	SOP
University of New Hampshire	HydroFIA	Attachment 4
University of Maine Darling Marine Center	Metrohm 877 Plus Titrino	Attachment 5
Bowdoin College	Customized apparatus	Attachment 6
Northeastern University Marine Science Center	Vindta 3C (Marine Analytics and Data)	Attachment 7
Massachusetts Institute of Technology	Custom built by Andrew Dickson Laboratory UCSD	Attachment 8
Woods Hole Oceanographic Institution	Metrohm 808 Titrando	Attachment 9
EPA AED-Narragansett Laboratory	Apollo SciTech Model AS-ALK2	Attachment 10
University of Connecticut	HydroFIA	Attachment 11

10. Equipment/Instrument Maintenance, Testing, Inspection and Calibration

A. Equipment and Instrument Maintenance, Testing, and Inspection

Analytical Equipment and/or Instrument	Maintenance Activity	Testing/ Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
Each laboratory analyzes total alkalinity using titrators	Check functioning of pumps, titrators, etc.	See SOPs	Daily and each batch	See SOPs	See SOPs	Laboratory managers	See SOPs

B. Equipment and Instrument Calibration

Analytical Equipment and/or Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
Each laboratory analyzes total alkalinity using titrators	Check accuracy compared to certified reference materials (CRMs)	2x daily, before and after batches	< +/- 10 µmol/kg of CRM	Repeat or check functioning of instrument and make adjustments	Laboratory managers	See SOPs

11. Field and Analytical Laboratory Quality Control (QC) Summary

Matrix	Analytical group or parameter	Quality Control (QC) Sample type	Frequency or Number of QC samples	Method or SOP QC Acceptance criteria or DQI goals (See Section 3)	Corrective Actions
Water	Total Alkalinity	Duplicates at low and high tides	Duplicates at low and high tide samples	1%	NA
Water	Total Alkalinity	Laboratory analysis duplicates	Duplicates of each sample	<+/- 10 µmol/kg	Re-run samples, inspect instrument, or adjust functioning of instrument
Water	Total Alkalinity	Laboratory CRMs	2x daily	<+/- 10 µmol/kg	Re-run samples, inspect instrument, or adjust functioning of instrument

12. Documents and Records

A. Document Control

The QA Manager will provide the QAPP to all key personnel, including the Project Manager, Laboratory Managers, and the Regional Coordinators.

B. Data Generation

A field datasheet (**Attachment 2**) will be generated for groups of samples collected by each monitoring organization. This sheet will also double as the chain-of-custody form.

The training will provide instructions in how to fill out this sheet.

Each group will have one datasheet with columns for different times of sampling.

We will provide pre-printed labels for bottles which will include data and sampling order.

The datasheet will be transported in a plastic bag with the samples, which will be in a cooler on ice. The samples will be preserved or stored at 4° C for immediate measurements.

C. Data Report Packages

Each partnering laboratory will prepare a data package for delivery to the project manager Parker Gassett and principal investigator Chris Hunt. Data entry will be performed by Emily Silva from NERACOOS. Each data package will include electronic and paper copies of the results. Each TA analyzer will have a screen to input sample label, salinity, temperature and instrument displays results for TA. Analyzer settings will also be written down in lab notebooks. The instrument creates a data file with these fields. Note that some laboratory instruments provide results in $\mu\text{mol per kg}$, and some are $\mu\text{mol per liter}$. For those laboratories providing results per volume, samples are weighed to convert to per kg basis.

The data package will include QC checks including results from the certified reference materials (CRMs), batch number for CRM and for certified titrants, standard deviation of replicates, number of replicates, QC flags. See laboratory SOPs **Attachments 4 to 11**) for additional information.

This file will be used to conduct quality control checks, such as for outliers, before delivery to the project manager.

D. Reporting Format

The final electronic database will merge ancillary data from field sites based on the field datasheets and the data files from the TA analyzers. Ongoing efforts through the Connecticut Department of Energy and Environmental Protection to generate GIS layers that compile Northeast coastal acidification monitoring, as well as the NERACOOS data platform are well suited to also host data.

E. Data storage

All electronic files and hard copies will be stored at the respective laboratories. Each laboratory will provide final QC'ed file to the Project Manager, Parker Gassett, and principal investigator Scientist Chris Hunt for final storage. The final data package will have flags for each data record.

Parker Gassett and Chris Hunt with the assistance of Emily Silva will be responsible for merging data files and for storing official versions of data.

13. Data Management

The field datasheets will be delivered from monitoring organizations to the regional coordinators to the partnering laboratories. Each laboratory will have different file formats, but we will ensure that each file has the minimum information that can be used to provide capability to merge. This includes calculated total alkalinity from the instrument, and bottle number, which can then be merged with the datafile generated from the field (ancillary) datasheets. Datasheets will then be delivered to the Project Manager (Parker Gassett). He will work with Emily Silva (NERACOOS), who will oversee transcription of data from field datasheets into an electronic database. Chris Hunt and Parker Gassett will check for errors including consistency of units, range of values and then merge the records from the laboratories datafiles into electronic data files. The datafiles will be keyed on sample bottle ID. Other ancillary data will be used to verify that merging is correct, such as sample time, location, and salinity, if available.

The regional coordinators and QA Manager will also assist in verifying these data.

Electronic files will be backed up routinely and stored at the University of Maine and NERACOOS under control of the Project Manager.

14. Reporting, Oversight and Assessments

Here is a list of reports and assessments expected to be produced related to the data generated. Each report will include information regarding QC and any corrective actions, or deviations from project plans, and assessment of quality of the data generated at each step of the way.

A. Reports

Type of Report	Frequency	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation	Report Recipient(s)
Lab data reports (data packages) from partnering laboratories including QC information and flagged data	Once	Fall 2019	Laboratory managers	Project manager (Gassett) and QA manager (Liebman)
Field summaries with datasheets, observations and deviations from project plan	Once	Late August, 2019	Regional coordinators	Project manager and QA manager
Draft data report	Once	Fall 2019	Project manager	Science advisory team
Final report	Once	January 2020	Project manager and Science Advisory Team	Funding agencies and public

B. Assessments

Assessment Type	Frequency	Person(s) Responsible for Performing Assessment	Person(s) Responsible for Responding to Assessment Findings	Person(s) Responsible for Identifying and Implementing Corrective Actions	Person(s) Responsible for Monitoring Effectiveness of Corrective Actions
Assess monitoring organizations sampling locations	August 22	Regional coordinators	Project manager and QA manager	Regional coordinators	QA manager and Science Advisory Team
Confirm chain-of-custody completed	August 23	Regional coordinators and laboratory managers	Project manager and QA manager	Regional coordinators	QA manager and Science Advisory Team

Assess completeness of data packages from laboratories	Fall 2019	Project manager and QA manager	Laboratory managers	Laboratory managers	QA manager
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15. Data Review and Usability

A. Data Review and Validation

Many of the data review steps have been described earlier at each step during the generation process. We will review data packages, and datafiles to determine whether data quality indicators are met, and whether data needs to be flagged.

Data files will be checked and sorted to determine whether sample id's align with appropriate times and locations, and whether sample id's align between sample locations and laboratory datafiles.

Data will be sorted to check whether ancillary data or laboratory data are outside expected ranges.

Data will be compared among laboratories to evaluate potential bias in laboratory analyses.

Salinity and total alkalinity data will be plotted to determine whether there are any outliers, or unexpected patterns.

Data will be flagged for many reasons, including:

- Sample time differs by more than 1 hour from expected low, medium, or high tide prediction.
- Bottle samples are clearly not filled or if there is debris in the bottle
- Salinity measurements outside expected range.

To validate data, we may need to review the field datasheets, interview monitoring organizations, evaluate chain-of-custody, review instrument datafiles, calculations of total alkalinity from titrators, corrective factors applied due to calibration from CRMs.

B. Data usability

Our reports will reconcile and address whether our project and data quality objectives are met, and whether there are limitations on the use of the data.

C. Data presentation

The draft and final reports will include data summaries. These will include descriptive statistics of results of total alkalinity, by region, estuary or embayment, tidal stage. We will analyze relationships statistically between salinity and total alkalinity by region, estuary or embayment, tidal stage.

16. References

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17. Attachments

Attachment 1. List of participating community water monitoring organizations

Attachment 2. Field Datasheet

Attachment 3. Combined Sampling SOP

Attachment 4. SOP from UNH for HydroFIA

Attachment 5. SOP from UMaine Darling Marine Center for Metrohm 877 Plus Titrino

Attachment 6. SOP from Bowdoin College for customized instrument

Attachment 7. SOP from Northeastern University for Vindta 3C

Attachment 8. SOP from MIT for custom built instrument

Attachment 9. SOP from WHOI Metrohm 808 Titrando

Attachment 10. SOP from EPA AED-Narragansett for Apollo SciTech

Attachment 11. SOP from UConn for HydroFIA