

Quality Assurance Project Plan for Long Term Ocean Acidification Monitoring of Long Island Sound

**Funded by:
Long Island Sound Study**


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Table of Contents

<u>Section</u>	<u>Page</u>
1.0 PROJECT MANAGEMENT	4
1.1 Title and Approval Page	4
1.2 Table of Contents	4
1.3 Distribution List	4
1.4 Project Organization	6
1.5 Problem Definition/Background	8
1.6 Project/Task Description and Schedule	10
1.7 Quality Objectives and Criteria for Measurement Data	10
1.7.1 Objectives and Project Decisions.....	13
1.7.2 Action Limits/Levels	13
1.7.3 Measurement Performance Criteria/Acceptance Criteria	13
1.8 Special Training Requirements/Certification	18
1.9 Documents and Records	18
1.9.1 QA Project Plan Distribution.....	18
1.9.2 Field Documentation and Records.....	18
1.9.3 Laboratory Documentation and Records	18
1.9.4 Quarterly and/or Final Reports	19
2.0 DATA GENERATION AND ACQUISITION	19
2.1 Sampling Design (Experimental Design)	19
2.2 Sampling & Analytical	20
2.3 Sample Handling and Custody.....	22
2.4 Analytical Methods.....	22
2.4.1 Field Methods	23
2.4.3 Laboratory Methods (Off-Site).....	24
2.5 Quality Control Requirements	24
2.6 Lab Instrument/Equipment Testing, Inspection, and Maintenance	25
2.7 Instrument/Equipment Calibration and Frequency.....	25
2.8 Inspection/Acceptance Requirements for Supplies and Consumables	26
2.9 Data Acquisition Requirements (Non-Direct Measurements).....	26
2.10 Data Management	26
3.0 ASSESSMENT AND OVERSIGHT	27
3.1 Assessments/Oversight and Response Actions.....	27
3.2 Reports to Management	27
4.0 DATA REVIEW AND USABILITY	27
4.1 Data Review, Verification, and Validation Requirements.....	27
4.2 Verification and Validation Methods.....	28
4.3 Reconciliation with User Requirements	28
5.0 REFERENCES	29
APPENDICES	31

1.0 PROJECT MANAGEMENT

1.1 Title and Approval Page (EPA QA/R-5 A1) - See page 1.

1.2 Table of Contents (EPA QA/R-5 A2) - See pages 3 - 4.

1.3 Distribution List (EPA QA/R-5 A3)

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Title: CTDEEP OA Monitoring QAPP

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Page 5 of 33

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1.4 Project Organization (EPA QA/R-5 A4)

University of Connecticut (UCONN)

Project & Analytical Lead

Dr. Vlahos will assist with overall management of the project and lead the chemistry components of the study, specifically her lab will be responsible for the analysis of samples. She will be the direct line of communication with both Long Island Sound Study (LISS) program managers, Connecticut Department of Energy and Environmental Protection (CT DEEP) Long Island Sound Water Quality Monitoring Program (LISWQMP) scientists and key lab personnel to coordinate efforts and ensure timelines are met.

CT DEEP

Project Manager

Matthew Lyman will be participating in all CT DEEP cruises and will work with the project team to collect and deliver samples to the analytical laboratory. Mr. Lyman will oversee training of permanent and seasonal staff that participate in the collection of samples for this project. As CT DEEP's database manager, Mr. Lyman will be responsible for overseeing data entry into the program database and participate in data sharing.

Quality Assurance (QA) Manager

Katie O'Brien-Clayton will be the CT DEEP QA lead. Mrs. O'Brien-Clayton will oversee logistics for this project including preparation of the Quality Assurance Project Plan (QAPP), Standard Operating Procedures (SOP)s, and coordination of sample delivery to ensure sample chain of custody. She will ensure that data collected for this project are of the highest quality; that data quality objectives are met, sample collections adhere to the QAPP, all personnel are properly trained in sample collection techniques, etc.

LISWQMP Program Oversight

Mary Becker, Supervising Analyst with the CT DEEP Monitoring Program, oversees all aspects of the CT DEEP Ambient Water Quality Monitoring Program.

Environmental Protection Agency Long Island Sound Study Office (EPA LISSO)

Ocean Acidification (OA) Subcommittee of the Water Quality Monitoring Workgroup (WQWG)

Cayla Sullivan, EPA LISSO Lead and Jim Ammerman, EPA LISSO WQWG Lead

The project will be discussed during regular meetings of the OA Subcommittee. This subcommittee will help assess project progress, discuss obstacles and make strategic recommendations where appropriate. The subcommittee will also advise the science team on the appropriate venues for data dissemination to reach target stakeholders and on strategies and possible future opportunities to maximize project utility.

Mentoring

Dr. Vlahos will be the direct advisor to Lauren Barrett & Mary McGuinness who are current Doctoral and

Masters students respectively. In Summer 2023 we will train incoming Doctoral student Abigail Whittington who will be trained and mentored throughout this study. Lauren and Mary have incorporated the baseline data into their research and Abby will make these data an integral part of her dissertation research. Summer undergraduate students through the National Science Foundation’s Research Experience for Undergraduates (REU) will work in Vlahos’s lab and assist on aspects of this project.

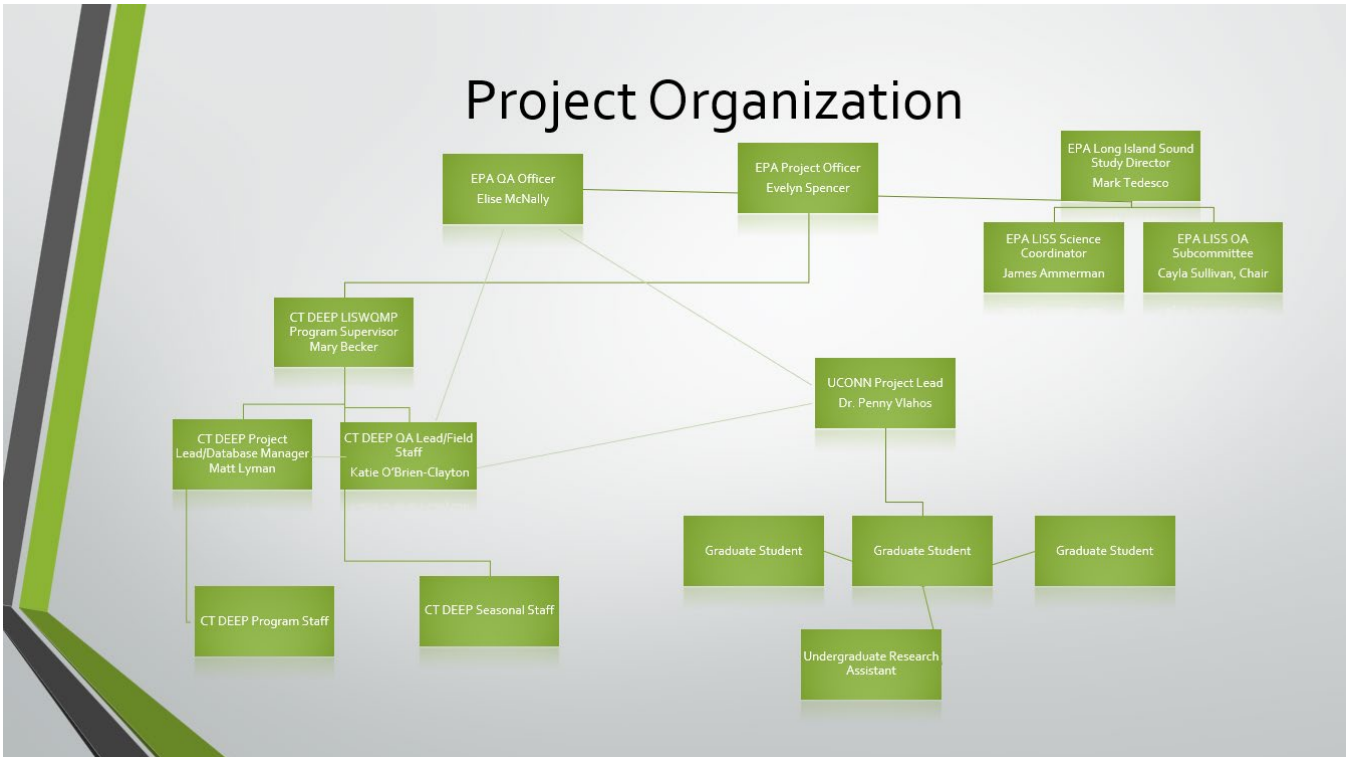


Figure 1-1. Organization Chart

1.5 Problem Definition/Background (EPA QA/R-5 A5)

Long Island Sound (LIS) is an urban estuary that is faced with increasing anthropogenic stressors and a shifting climate. Global stressors including increasing atmospheric carbon dioxide (CO₂) and acidification, climate shifts and warming waters cannot be managed at the local level, however; anthropogenic nitrogen loads to LIS and eutrophication can. It is critical to develop a baseline and to understand the Sound's ability to respond to these stressors.

There is a need for understanding the trends in LIS carbonate chemistry in terms of the system's buffering capacity (total alkalinity) and trends in acidification (pH). Total Alkalinity (TA) describes the system's ability to withstand changes in pH due to rising CO₂ levels and eutrophication (the other CO₂ problem, Wallace et al., 2014). Low alkalinity freshwater discharge and eutrophication associated with anthropogenic nitrogen loading contribute to reduced buffering capacity and leave the Sound highly vulnerable to ocean acidification due to a strong economic reliance on shellfish aquaculture (Ekstrom et al., 2015, Rheuban et al., 2019, Wang et al., 2013). Recent studies to understand the biogeochemistry of LIS include the RESPIRE project and the ALISE project (Vlahos and Whitney 2017, Vlahos et al., 2020a, Byrd et al., 2020) which examined LIS Proper and a subset of LIS embayments, respectively.

This project will collect water column samples that will be analyzed for three carbonate system parameters: total alkalinity, pH, and dissolved inorganic carbon (DIC). These data are also intricately coupled to currently measured parameters in the LIS Water Quality Monitoring Program (dissolved oxygen (DO), temperature, salinity) and will add important trends to this time series. In addition, these data will help identify areas in LIS where there may be critical stress on shellfish that rely on carbonate to build and maintain their shells.

The Long Island Sound Study (LISS) has funded multiple projects related to nutrient bioextraction over the last few years. Nutrient bioextraction utilizes aquaculture to grow and harvest shellfish and seaweed to remove excess nutrients from Long Island Sound and its coastal waters (LISS, undated a). Details on the LISS Bioextraction Initiative can be found on the [website](#). Data collected as part of the OA monitoring program will be important for the success of the Initiative.

The [Connecticut Shellfish Initiative](#) was launched in 2014 to promote the growth of shellfish beds and shellfishing. The Initiative sought to identify and remove barriers to commercial and recreational harvesters and raise public awareness about CT's shellfish resources (Getchis, et. al., 2016). There are over 50 companies employing more than 300 people, generating more than \$16 million for the Connecticut economy. Climate change (increasing temperatures, sea level rise, precipitation pattern changes, ocean acidification, and severe weather) pose a significant threat to infrastructure, production, and sales for the shellfishing industry. A product of the Initiative is the recently released [Connecticut Shellfish Restoration Guide](#) which utilizes best available scientific resources to provide a vision to *“Restore, manage, and conserve shellfish habitats to improve environmental, economic, and societal*

benefits known as “ecosystem services”. The five key ecosystem services include: 1. Shellfish Production 2. Coastal Habitat Provision 3. Improved Water Quality 4. Fisheries Production 5. Shoreline Stabilization (Getchis, et. al., 2022). The Guide includes associated priority actions, decision-making tools, regulatory information and best management practices, and recommended high-priority restoration projects for future funding. Recommendations 13, 14, and 15 specifically relate to water quality monitoring, OA monitoring, and climate change research on shellfish habitats. Data collected as part of the OA Monitoring program will address restoration recommendations.

Additionally, The [Long Island Sound Study Climate Change and Sentinel Monitoring Program](#) is charged with quantifying climate change impacts to Long Island Sound and providing managers with data to respond to those changes (LISS, undated b). The Strategy developed for the program identified acidification as a sentinel to be monitored, along with core water quality parameters of salinity, temperature, and pH. Data collected as part of this project will assist furthering the strategy and quantifying climate impacts to the Sound.

1.6 Project/Task Description and Schedule (EPA QA/R-5 A6)

Expected Outputs and Outcomes

- 1) A formal EPA QAPP designed according to "Elements of a Quality Assurance Project Plan (QAPP) For Collecting, Identifying and Evaluating Existing Scientific Data/Information" for use by the broader scientific and management community.
- 2) A time series of TA, spectrophotometric pH and DIC across the central LIS axis.

Table 1.6.1. - Project timeline and outcomes.

Tasks / Activities / Milestones	Related Project Objective(s)	Funding Year 1												Funding Year 2											
		Beginning Month and Year: October 2022																							
		Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Month 9	Month 10	Month 11	Month 12	Month 13	Month 14	Month 15	Month 16	Month 17	Month 18	Month 19	Month 20	Month 21	Month 22	Month 23	Month 24
LISS OA Subcommittee Meeting	1-6	█			█			█				█													
Complete EPA QAPP	1-6	█	█	█	█	█	█	█																	
Order equipment	1-3	█	█	█																					
Conduct TA, DIC, pH surveys and analyses	2,6																								
Reporting																									

1.7 Quality Objectives and Criteria for Measurement Data (EPA QA/R-5 A7)

There primary measurement parameters proposed to be collected under this QAPP are Total Alkalinity, Dissolved Inorganic Carbon and Spectrophotometric pH. Secondary measurement data required for interpretation of analytical results generated under this project include salinity, temperature, and dissolved oxygen. Data Quality Objectives and Criteria for these secondary measurement data are covered in the EPA approved LISWQMP QAPP (QA Tracking #22137, CT DEEP 2022) and are presented in Table 1-2.

The overarching Measurement Quality objective is to collect field observations and complete chemical analysis with the same accuracy and precision goals as the CT DEEP Long-Term Monitoring Program for LIS (CTDEEP, 2022), the LIS RESPIRE Program (Vlahos et.al., 2019), and the ALISE Project. Common Data Quality Indicators (DQI) are described in Table 1-1 below (excerpted from EPA 2019). DQIs identified for this project include those commonly referred to as PARCCS (Precision, Accuracy, Representativeness, Comparability, Completeness, and Sensitivity). Section 1.7.3 discusses

measurement acceptance criteria for accuracy and precision for each of the parameters collected under this project (i.e., TA, DIC, spectrophotometric pH).

Table 1-1. Common Data Quality Indicators

Data Quality Indicator (DQI)	Description
Precision	The degree of agreement among repeated measurements or observations of the same variable under the same or very similar conditions
Bias	The systematic or persistent distortion of a data collection process resulting in error in one direction
Accuracy	The degree to which a measured or observer-determined value agrees with a known or reference value; includes a combination of random error (precision) and systematic error (bias)
Representativeness	The degree to which data represent the characteristic of a population being assessed
Comparability	Confidence that data can be compared to or combined with other data collected for similar purposes
Completeness	A measure of the amount of valid data obtained from a data collection system compared to the amount that was expected to be obtained under correct, normal conditions
Detectability/ Sensitivity	A measure of the sensitivity and specificity of the sampling design, measurement procedures, instrumentation and/or data collection personnel in detecting true differences in a target variable at ambient levels or when the measurement or observation of a target variable is dependent upon detecting a rare, cryptic or secretive organism

Representativeness: Sampling occurs monthly, year-round at fixed station locations, regardless of tide stage. These locations were chosen based on historical sample locations and data, basin morphology of the Sound, and depth strata to be representative of ambient conditions Sound-wide. The Spatial Coverage objective is to collect observations at eastern, central, and western LIS stations from surface and bottom depths. This level of spatial coverage is required to characterize differences among regions of LIS and the adjacent coastal waters, resolve the lateral (across-estuary) variations in measured variables, and assess vertical variability through the water column. The Temporal Coverage objective is to collect observations over tidal periods and year-round to assess seasonal variability. Specific tide stage is not targeted. Tidal phase is recorded post survey on field data sheets by the survey crew utilizing National Oceanic and Atmospheric Association (NOAA) Tide Charts from three tide stations (Kings Point, NY, Bridgeport, CT, and Thames River, CT).

Comparability: Program sampling procedures are based on previous data collection efforts of the Long Island Sound Study. Consistent field and laboratory procedures, well-documented by the appropriate SOPs, help ensure consistent and reproducible data.

Completeness: With regard to analytical laboratory measurements for TA, DIC, and pH, the goal for record completeness is 100% of the samples received. The goal/acceptance criteria for secondary parameters (salinity, temperature, dissolved oxygen) is 95%. Completeness is affected by cancelled cruises and missed stations during a cruise (i.e., expected samples are never collected), and by field or laboratory accidents or malfunctions that render collected samples insufficient for any or all analyses, or that render analytical results unattainable or unreliable. Missed station visits are generally due to weather related conditions and lack of vessel or crew availability for rescheduling, or other vessel issues, including availability or where the use of an alternate/backup vessel meant limitations to sampling.

Sensitivity: Tables 1-3 through 1-5 provide the manufacturer's specifications related to sensitivity, accuracy, and precision for instruments utilized to conduct laboratory analyses of primary parameters (TA, DIC, spectrophotometric pH). Table A7-3 in the LISWQMP QAPP (CTDEEP 2022) provides the manufacturer's specifications for the Yellow Spring's Instrument (YSI) multiparameter sonde utilized to collect secondary parameters (DO, salinity, temperature).

1.7.1 Objectives and Project Decisions

- 1) Measure three of the four key biogeochemical parameters (total alkalinity (TA), dissolved inorganic carbon (DIC), and pH at ten (10) Long Island Sound (LIS) water quality stations to characterize the carbonate system in relation to ocean and coastal acidification.
- 2) Calculate aragonite saturation state
- 3) Provide data to stakeholders, managers, and industry so they can make informed decisions and undertake pertinent actions to protect resources and economies

1.7.2 Action Limits/Levels

Shellfish, crustaceans, and other organisms utilize calcium carbonate to create their shells and exoskeletons. Aragonite saturation (Ω) is a measure of the carbonate ion concentration in seawater. It is often used to track ocean acidification. When the aragonite saturation state drops below 3 shellfish and other shell making organisms become stressed. When aragonite saturation falls below 1, shells begin to dissolve.

- Aragonite saturation state <3 - classes of organisms become stressed
- <1 conditions are critical to calcifying organisms and shells begin to dissolve.

1.7.3 Measurement Performance Criteria/Acceptance Criteria

This QAPP is designed to ensure that accurate and precise data are being generated. Quality Control (QC) measures include those actions which are taken in the laboratory to verify that the measurement system is in control (*e.g.*, instrument calibration; the analysis of reference standards; replicates, and blanks). The Quality Assurance (QA) program is designed to manage sample handling, documentation, and custody; proper data generation; and quality control actions. The QA program primarily tracks and monitors the fate of a sample from collection to data submission allowing the Project Manager and technical staff to assure proper sample analysis through appropriate methods, and that the necessary QC measures have been taken to ensure that representative data of definable quality have been produced.

Analytical laboratory procedures, including the key elements of laboratory quality control are documented in laboratory-specific documentation (Dickson et al., 2007). A number of routine quality control checks are analyzed with each batch of samples, including continuing calibration verification, calibration blanks, laboratory duplicates, and spike sample analyses. The goal for each sample batch is to run each QC check on 10% of samples. Field blanks (prepared randomly once each cruise day to evaluate contamination potential) and field duplicates (replicates taken in rapid succession to estimate field precision) are also provided to the laboratory, at a rate of at least one per ten samples (10%).

Determination of accuracy will be accomplished by evaluating a continuing series of spiked samples. Percent recovery in the range of 85 to 115% is considered to be acceptable providing all other QC conditions are within acceptable limits. Accuracy of analysis will also be assessed by analyzing standard reference materials obtained commercially.

Determination of precision will be accomplished by evaluating a continuing series of replicated samples. The Relative Percent Difference (RPD) is used to evaluate the long-term precision of the method for each parameter. A control limit of +/- 15% RPD shall be used to define acceptable precision. When the precision is not met then data will be flagged and additional replicates will be added to follow up surveys.

Certified reference material (CRM) provided by Dr. Andrew Dickson (Marine Physical Laboratory, Scripps Institute of Oceanography, La Jolla, California) will be utilized for calibration and in the determination of accuracy and precision for TA and DIC.

Table 1-2 provides the accuracy and precision goals for laboratory analyses. All analytical precision is assessed by RPD.

Table 1-2 Laboratory Analyses Quality Objectives and QA Sample Information.

Variable	Accuracy Goal	Precision Goal	QA Sample Type	QA Frequency	Data Generated
Alkalinity (TA)	95-105%	<5%	Standards, lab and field duplicates; biannual audit	Per batch; each survey	Relative accuracy and precision; estimate of field contamination
Dissolved Inorganic Carbon (DIC)	85-115%	15%	Standards, lab and field duplicates; biannual audit	Per batch; each survey	Relative accuracy and precision; estimate of field contamination
pH (Spectrophotometric)	99-101%	0.01%	Standards, lab and field duplicates; biannual audit	Per batch; each survey	Relative accuracy and precision; estimate of field contamination

Accuracy and precision goals for ancillary measured parameters are provided in Table 1-2, along with quality assurance sample types. Accuracy and precision goals are based on instrument manufacturer or analytical laboratory specifications, or historical data or experience. Most variables have one or more QA/QC samples associated with them. Tidal phase is based on time on station. This will be tracked and must be taken into consideration in metadata.

Tables 1-3 through 1-5 provide the manufacturer specifications for field and laboratory equipment.

Table 1-3 Measurement quality objectives and quality assurance sample information for field water column observations.

Variable	QA Sample Type	Frequency of QA	Data Generated
Depth, temperature, DO, Conductivity/ Salinity, pH, turbidity, Total Algae, fDOM	Performance verification at certified calibration facility	Annually	response vs. calibration standards; annual drift
Depth	QC check against vessel's depth finder	Every cast	Difference between profile station depth and on-board depth finder
Temperature	QC check against NIST certified thermometer	At least biennially	Difference between probe and standard
Conductivity/ Salinity, pH, turbidity, Total Algae, fDOM	Calibration against standards	At least monthly; always prior to cruise	Difference between probe and standard
Dissolved Oxygen	Calibration	At least monthly; always prior to cruise	100% saturated air

Table 1-4 Manufacturer's Equipment Specifications- ControsHydroFIA TA Analyzer

TECHNICAL SPECIFICATIONS			
Detector	VIS absorption spectrometry, temperature stabilized, benchtop system	Measuring range:	
		- dynamic	400 $\mu\text{mol kg}^{-1}$
		- standard	2000 $\mu\text{mol kg}^{-1}$ to 2400 $\mu\text{mol kg}^{-1}$
Field application	Surface water	Resolution	0.1 $\mu\text{mol kg}^{-1}$
Dimensions	480 x 400 x 322 mm	Initial accuracy	$\pm 5 \mu\text{mol kg}^{-1}$
Weight	25 kg	Precision	$\pm 2 \mu\text{mol kg}^{-1}$
Temperature range ambient	+5 °C to +30 °C	Measurement cycle	<10 min
Salinity range	20-37 psu	Power supply	100 VAC to 240 VAC
		Data interface	Ethernet, RS-232

Specifications subject to change without notice.

Table 1-5 Manufacturer’s Equipment Specifications- Agilent Cary 60 UV-Vis Spectrophotometer

Specifications

Depth	567 mm
Height	196 mm
Light Source	Xenon flash lamp (80 Hz)
Maximum Scanning Speed	24,000 nm/min
Photometric System	Double beam
Power Consumption	Mains supply of 100 - 240 volts AC and frequency 50 - 60 Hz
Spectral Bandwidth	1.5 nm
Wavelength	190 - 1100 nm
Width	477 mm
Z-height	20 mm

Table 1-6 Manufacturer’s Equipment Specifications- Shimadzu TOC-V Analyzer

Model	TOC-VWS	TOC-VWP
Measurement method	wet oxidation/NDIR	
Operation method	standalone	PC-controlled
Measured items	TC,IC,TOC,NPOC	
Applicable samples	aqueous sample	
Measurement range (mg/L)	TC: 0 to 3500 IC: 0 to 3500	
Detection limit	0.5µg/L	
Measurement accuracy (reproducibility)	CV1.5% max. (CV2% max. at 1000mg/L or higher)	
Measuring time	TC:approx. 4mins. IC:approx. 4mins.	
Sample injection	automatic injection	
Sample injection volume	350 to 20400 µL variable	
IC pre-treatment	Automatic internal acidification and sparging	
Automatic dilution	dilution factor 2 to 50	
Gas consumption	approx. 3000 L/month (operating conditions: 8 hours/day x 5days/week)	
Ambient temperature range	5 to 35°C	

Table 1-7. Manufacturer's Equipment Specifications- Apollo DIC Analyzer with a Multi-Sampler *Model AS-C6L*

- Precision: $\pm 0.1\%$ for seawater (or $\pm 2 \mu\text{mol/kg}$)
- Sample Volume: 0.5 – 3.5 mL per analysis
- Time: ~ 3 minutes per analysis
- Software: *Apollo SciTech software included*
- Communication: RS-485, USB
- Power Supply: *Universal (100 – 240 V)*
- Carrier Gas: *Compressed air, ~ 16 psi (1.1 atm)*
- Environment: *Shipboard or land-based laboratory*

Table 1-8. Manufacturer's Equipment Specifications- Metrohm 905 Autotitrator for low salinity TA

	904 Titrande	905 Titrande	906 Titrande	907 Titrande
Dosing elements	1 integrated Dosimat with 806 Exchange Unit	Space for two 800 Dosinos with 807 Dosing Unit	1 integrated Dosimat with 806 Exchange Unit	Space for two 800 Dosinos with 807 Dosing Unit
Attachment of additional dosing elements	Up to 9 x 805 Dosimat with 806 Exchange Unit Up to 12 x 800 Dosino with 807 Dosing Unit			
Intelligent Exchange Unit/Dosing Unit with integral Data Chip	yes			
Dosing steps per cylinder volume (resolution)	904 Titrande with 805 Dosimat: 20'000	905 Titrande with 800 Dosino: 10'000	906 Titrande with 805 Dosimat: 20'000	907 Titrande with 800 Dosino: 10'000
Operation, dialog	Touch Control or tiemo™			
Stirrers, titration stand	4 x 801 Magnetic Stirrer or 4 x 802 Rod Stirrer with 804 Titration Stand or 803 KF Titration Stand			
Attachment of Dosimats, Dosinos, stirrers	4 MSB connectors (Metrohm Serial Bus, Daisy Chain)			
Sample Changer attachment	1 sample changer via USB			
Attachment of balances, printer, PC, PC keyboard, barcode reader	Via 2 USB Slave Ports, RS-232/USB Box (option)			
Attachment of additional measuring modules (867 pH Module or 856 Conductivity Module)	yes			
Temperature sensor	Pt 1000 or NTC			
Differential amplifier	Option			
Real-time curve display on Touch Control (90 mm x 120 mm) or PC screen	yes			
DET Dynamic Equivalence-point Titration	yes			
MET Monotonic Equivalence-point Titration	yes			
SET Titration to a preset endpoint with automatic conditioning	yes			
KF Volumetric Karl Fischer titration with automatic conditioning	no		yes	
STAT Titration to a preset control point and maintaining the corresponding measured value	no		yes	
MEAS Measuring mode for pH, U/mV, T/°C	Resolution: 0.001 pH, 0.1 mV, 0.1 °C; Measuring interval: 100 ms			
MEAS CONC Direct measurement using ISE and calculation of concentration	yes			
CAL Calibration with automatic buffer recognition	yes			

https://www.metrohm.com/en_us/products/2/9050/29050010.html

1.8 Special Training Requirements/Certification (EPA QA/R-5 A8)

The Primary Investigators (PI) each have more than fifteen years of experience conducting field operations, making water quality measurements, collecting water samples, and completing the analysis required in this project. PI Vlahos specializes in biogeochemical analysis. The Department of Marine Sciences has dedicated laboratory managers that oversee students in laboratory methods and chemical analysis. All project members undergo mandatory laboratory safety training offered every year by the University both on site and through online resources. The graduate students participating in this project will be trained in each field or analytical method they conduct. This includes training in sample collection, sample handling, accurate record keeping, and chemical analysis methods. The students will be supervised at least the first five times they conduct a new task and will not be allowed to proceed unsupervised until they have demonstrated proficiency. Training will be documented as part of each student's graduate research courses.

1.9 Documents and Records (EPA QA/R-5 A9)

1.9.1 QA Project Plan Distribution

The QAPP will be distributed to the people on the Distribution List (Section 1.3) electronically (as a PDF file) via email once approved and after any subsequent revisions. The QAPP also will be posted on the CT DEEP website.

1.9.2 Field Documentation and Records

Data collected in the field includes measurements of water temperature, dissolved oxygen concentration, salinity, and pH (See Section 2). Ancillary data such as weather, tide stage, cloud cover estimates, and latitude/longitude are also recorded. Data are recorded and stored to the multiparameter sonde in real-time. Field data are uploaded from the sonde to a program laptop as well as to the CT DEEP data folders on a secure server immediately following the survey. Servers are backed up nightly. After processing, data are uploaded to the Program database (AWX), as well as the UCONN ERDDAP and EPA Water Quality Exchange (WQX) for public access through the Water Quality Portal.

Data are also recorded on hard copy field data sheets and on electronic field data sheets using ESRI's Survey 123. CT DEEP is in the process of developing standard operating procedures and quality assurance checks for Survey123 data entry and will be phasing out hard copy data sheets. Hard copy data sheets are also scanned and retained as PDFs according to the CT DEEP Records Retention Policy.

1.9.3 Laboratory Documentation and Records

The Vlahos laboratory maintains an inventory of all solvents, reagents and standards at all times on both the laboratory computer and as a printed hardcopy. Samples are all logged into a project spreadsheet that records sample ID, time and date and the name of the analyst and in students' personal laboratory books. Analysis on instrumentation generates a permanent data file that is stored in the respective project folder in either the Vlahos laboratory or the shared Smaller Laboratory facility in the UCONN Marine Sciences Building. Following analysis data are also stored on Vlahos's desktop and the responsible analyst's

desktop, both of which are password protected. All project data are compiled, emailed to CT DEEP for upload to their AWX database and ultimately stored on the WQX and Water Quality Portal. Values with uncertainties will be provided to CT DEEP by UCONN. These records will be archived with redundancy indefinitely.

Data will be uploaded to AWX by CT DEEP upon receipt from the analytical lab. As data will be received from the lab in Excel spreadsheets formatted to CT DEEP specifications, no data processing or manipulation will be performed. Data from AWX are uploaded to WQX monthly.

1.9.4 Quarterly and/or Final Reports

Project activities and research results will be included in quarterly and annual reports electronically submitted (as PDF file) to CT DEEP.

DATA GENERATION AND ACQUISITION

2.1 Sampling Design (Experimental Design) (EPA QA/R-5 B1)

The Connecticut Department of Energy and Environmental Protection on behalf of the Long Island Sound Study estuary program, has conducted a LIS Water Quality Monitoring Program since 1991, with most stations sampled since 1995. Samples are collected monthly from 17 sites year-round by researchers aboard the R/V John Dempsey. Sampling frequency increases to bi-weekly in mid-June through September as does resolution (48 stations). Sampling includes the collection of grab samples for nutrient analyses and BOD, net twos for phyto- and zooplankton community analyses, and in situ profile measurements for DO, temperature, pH, turbidity, chlorophyll a and blue green algae phaeophytin. Additional details can be found in the 2022 QAPP (Tracking Number 22137, CT DEEP 2022).

Figure 2-1 illustrates the locations of 10 stations from which grab samples will be collected and analyzed for TA, DIC, and pH (circled in black). Stations A4, C1, D3 and 09 will be sampled during the Western Sound cruise day, stations E1, 15 and F2 will be sampled during the Central Sound day, and stations H4, I2 and K2 will be sampled on the Eastern Sound day. All OA parameters will be collected monthly during the water quality cruises. The 10 sampling stations were chosen to sample along the east-west and north-south axes of the Sound encompassing shallow and deep stations. Sampling will be conducted year-round with samples collected from surface (defined as 2m) and bottom depths (defined as 5m above the sediment/water interface). A total of 48 sample bottles will be filled per survey (10 stations X 2 depths X 2 bottles) plus one duplicate (2 bottles X 2 depths) and one field blank (2 bottles per depth). See section 2.2 for more details. Table 2-1 provides station information including the latitude and longitude.

Table 2-1. Sampling Station Information

Station	Station Depth (m)	Latitude	Longitude	Sampling Record	Rationale for Sampling Design
A4	32.6	40 52.35N	73 44.05W	8/94-present	Across LIS central axis/Execution Rocks
C1	19.8	40 57.35N	73 34.82W	12/94-present	Across LIS central axis/Oyster Bay
D3	40.9	40 59.63N	73 24.68W	2/91-present	Across LIS central axis/Eaton's Neck Point
09	0	41 04.25N	73 20.17W	6/94-present	Across LIS central axis/Nissequogue River
E1	38.1	41 01.16N	73 17.48W	12/94-present	Western LIS north-south axis/Saugatuck River
15	15.3	40 55.88N	73 13.27W	6/94-present	Western LIS north-south axis/Smithtown Bay
F2	19.7	41 04.82N	73 09.92W	12/94-present	Across LIS central axis/New Haven Harbor
H4	23.7	41 06.10N	72 56.04W	6/94-prsent	Across LIS central axis/Duck Island
I2	27.3	41 08.25N	72 39.30W	1/91-present	Across LIS central axis/Plum Gut Harbor
K2	37.7	41 14.06N	72 15.95W	7/94-present	Across LIS central axis/Connecticut River

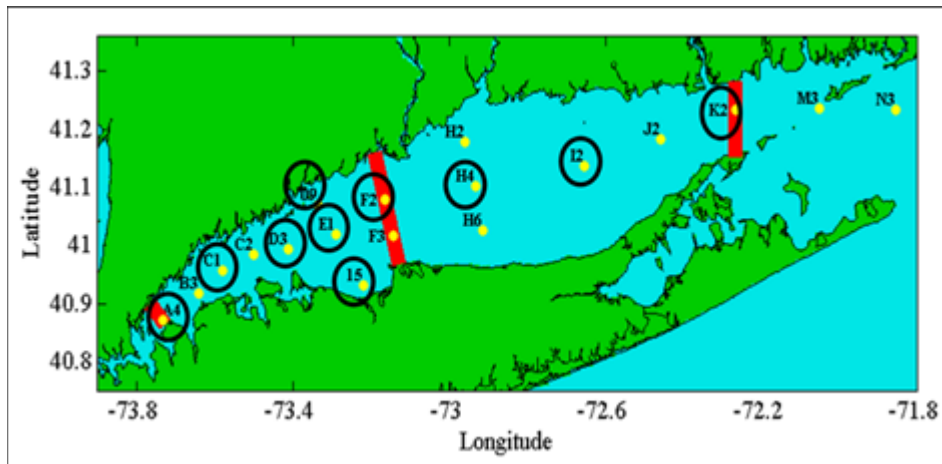


Figure 2-1. Site Map with Sampling Locations. The 17 CT-DEEP year-round monitoring stations are shown (yellow dots) and 10 stations at which TA, pH, and DIC (circled) will be conducted. Sampling is designed to achieve spatial coverage across the entire Sound.

2.2 Sampling & Analytical Methods (EPA QA/R-5 B2)

For this project, grab samples will be collected utilizing 5L Niskin bottles mounted to a General Oceanic Rosette sampling array. Sample bottles (250 ml borosilicate glass vials) will be filled by CT DEEP staff in the field directly from the Niskin bottles using gas vapor tubing supplied by the Vlahos lab, preserved with saturated mercuric chloride, stored in coolers, and delivered to the Vlahos lab along with Chain of Custody forms following the completion of the survey. Samples will be collected from 2 meters below the surface (surface) and 5 meters above the sediment (bottom). Two replicates will be collected per

station depth. The samples will be field filtered to make results comparable to samples collected by other LIS OA monitoring programs (i.e., the United States Geologic Survey). Analyses will be conducted in the Vlahos Lab at UCONN Marine Science building. Ancillary data (i.e., dissolved oxygen, temperature and salinity) necessary for the analyses will be obtained from in situ profile data (upcast) utilizing the CT DEEP YSI mounted to the rosette array. Grab sampling will follow CT DEEP standard operating procedures and be performed under the EPA approved QAPP (QA Tracking Number 22137; CT DEEP, 2022).

A detailed description of sample collection methods is provided in the Standard Operating Procedure supplied by the Vlahos Lab (Appendix A) and Section 2.4.1. Analytical Methods will follow Dickson et. al., (2007) [*Guide to Ocean CO2 Measurements*](#) and Carter et. al., (2013). Accuracy and precision will be calibrated daily using certified reference material (CRM) provided by Dr. Andrew Dickson (Marine Physical Laboratory, Scripps Institute of Oceanography, La Jolla, California).

Table 2-2. OA Sample Field Method, Analytical Method, Containers, Preservation, and Holding Times Requirements. Two replicates will be collected per station depth.

Analytical Method	Preservation at the time of collection	Holding Times Requirements	Field Method	Analytical Method	Detection Limit
DIC	HgCl ₂	Within 60 days	Directly collected into vial using gas tubing with inline filter and fixed with mercuric chloride and 1% headspace.	Apollo DIC Analyzer (non dispersive analyzer; EPA 415.1)	± 3 uM
alkalinity	HgCl ₂	Within 60 days	Directly collected into vial using gas tubing with inline filter and fixed with mercuric chloride and 1% headspace.	Metrohm 905 autotitrator and/or ControsFIA TA Analyser (for samples of salinities over 20 PSU) following Dickson et. al., (2017)	± 2 uM
pH	HgCl ₂	Within 48 hours	Directly collected into vial using gas tubing with inline filter and fixed with mercuric chloride and 1% headspace.	Agilent Cary 60 UV-Vis systems spectrophotometer and m-cresol purple indicator dye following Carter et. al., (2013).	± 0.0002

2.3 Sample Handling and Custody (EPA QA/R-5 B3)

Onboard sample handling will be supervised by PI Lyman. Samples will be labeled, preserved and placed in onboard coolers. Upon return to shore, samples will be stored preserved at room temperature until chemical analysis. Samples will be delivered to the Vlahos lab at UCONN Avery Point monthly, following completion of regular DEEP water quality surveys. Samples will be accompanied by Chain of Custody sheets (Appendix B). During laboratory analysis, samples, analysis times, and any corresponding notes will be kept in the project spreadsheet (Section 1.9.3). Sample handling in the laboratory will be by PI Vlahos, Laboratory Coordinator Koerting, and trained graduate students working on the project. Specifics on the samples, containers, preservation methods, and holding times are included in Table 2-3.

2.4 Analytical Methods (EPA QA/R-5 B4)

Analytical methods are summarized in Table 2-2. Analytical Methods will follow Dickson et. al., (2007) *Guide to Ocean CO2 Measurements* and Carter et. al., (2013).

Alkalinity: *Dickson SOP 3b* The method is suitable for assaying oceanic levels of total alkalinity (2000–

2500 $\mu\text{mol kg}^{-1}$). Lower values may be encountered in coastal and surface polar waters. This method should be suitable for the lower range with a smaller initial acid addition. TA will be measured using either a [CONTROS HydroFIA TA Analyser](#) (salinities over 20 PSU) or a Metyrohm 905 Autotitrator owned by the Vlahos lab. From the manufacturer's website: *The CONTROS HydroFIA® TA is a flow through system for the determination of the total alkalinity in seawater. It can be used for continuous monitoring during surface water applications as well as for discrete sample measurements. A defined amount of seawater is acidified by injection of a fixed amount of hydrochloric acid (HCl). After acidification the generated CO₂ in the sample is removed by means of a membrane based degassing unit resulting in a so-called open-cell titration. The subsequent pH determination is carried out by means of an indicator dye (Bromocresol green) and VIS absorption spectrometry. Together with salinity and temperature, the resulting pH is directly used for the calculation of total alkalinity.*

DIC: Dickson SOP 2 DIC samples will be collected in acid cleaned, pre-combusted 20 mL glass vials, filled leaving ~1% headspace to allow for expansion, preserved with 10 μL of saturated mercuric chloride and crimped with gas tight aluminum caps with PTFE seals. Bottles will be refrigerated at 4°C in the dark and analyzed at UCONN using an Apollo DIC analyzer.

The method is suitable for the assay of oceanic levels of total dissolved inorganic carbon (1800–2300 $\mu\text{mol kg}^{-1}$) and also for higher levels such as are found in the Black Sea (3800–4300 $\mu\text{mol kg}^{-1}$).

pH: The concentration of hydrogen ion (pH) will be determined spectrophotometrically using m-cresol purple indicator dye following Carter et al. (2013) which improved upon Dickson's method. Analysis will be conducted using an Agilent Cary 60 UV-Vis spectrophotometer to have a dedicated instrument for discrete pH measurements that parallel discrete TA measurements. Samples will be T equilibrated in the instrument's thermostatted cell holder at 25°C and precision and accuracy using triplicate samples from the same Niskin bottle and TRIS buffers. The precision of the pH measurements is estimated to be approximately ± 0.0014 (Woosley et al., 2017). Further details on the methods and quality control are described in Woosley et al. (2017).

Aragonite Saturation: The omega value (Ω) will be calculated using the PyCO2SYS Python package (Humphreys et al., 2022). The empirical constants used in these calculations were those of Lueker et al. (2000), Dickson et al. (1979), Dickson et al. (1990), and Lee et al. (2010).

2.4.1 Field Methods

Field methods for the collection of salinity, temperature and dissolved oxygen will follow methods detailed in the 2022 LIS WQMP QAPP (Long Island Sound Ambient Water Quality Monitoring Program, Water Quality and Hydrographic Surveys, Standard Operating Procedures Manual, 2022 (Program SOP) (Appendix A); CT DEEP 2022). These parameters are needed for the TA analysis. Generally, *in situ* profiles will be taken using a Yellow Springs Instrument (YSI) multiparameter sonde deployed on a General Oceanics Rosette sampling array. The array is lowered at a constant speed to the bottom. Data are saved to the sonde and uploaded to a CT DEEP laptop computer following the survey.

Profiles are viewed in real-time and measurements recorded on field data sheets by Ms. O'Brien-Clayton or a trained LIS seasonal employee. Field measurements needed for the TA analysis will be transcribed to the chain of custody form that will accompany the samples to the Vlahos lab.

TA, pH, and DIC samples will be collected as grab samples on the profile upcast using 5L Niskin bottles mounted to the Rosette sampling array. The Niskins are triggered remotely from the shipboard laboratory. Gas sampling tubing provided by the Vlahos lab will be attached to the Niskin bottle outlet. An inline filter will be attached to the tubing. Sample collection vessels will generally be pre-labeled from the Vlahos lab. Samples will be collected in one 250 mL borosilicate glass bottle. All samples must be preserved with 100 uL saturated mercuric chloride (minimum 0.02% by volume). 1% headspace should be left. The bottles should be sealed with Apiezon grease, rubber band, and hose clamp to inhibit gas exchange. See Appendix A- OA Field Collection SOP for details.

2.4.3 Laboratory Methods (Off-Site)

See Table 2-2. Analytical Method, Containers, Preservation, and Holding Times Requirements. Methods will follow Dickson, et.al., (2007) *Guide to Best Practices to Ocean CO₂ measurements*, and Carter et. al., (2013). Sample analysis will occur in the following order: DIC, pH, then TA.

2.5 Quality Control Requirements (EPA QA/R-5 B5)

Effective quality control for this project relies on the proper inspection, maintenance, and calibration of field and laboratory instrumentation as described in Sections 2.6 and 2.7. The precision scientific instrumentation that will be used will satisfy the Measurement Quality Objective as long as they are properly functioning and calibrated. The frequency of quality control activities is either on a pre-survey basis or on the recommended instrument calibration schedule (as described below). Field surveys, sample collection, and laboratory analysis will be conducted only by trained personnel under the supervision of the PIs, and/or laboratory coordinator. Field and laboratory logs will include a record of quality control activities and requisite actions taken.

Accuracy and precision will be calibrated daily using certified reference material (CRM) provided by Dr. Andrew Dickson (Marine Physical Laboratory, Scripps Institute of Oceanography, La Jolla, California). Dickson et. al., (2007) SOPs include quality control requirements that will be followed by the Vlahos lab.

A field duplicate will be collected and sent to the Vlahos lab for analyses from station A4 or E1. A field blank will also be collected once per cruise. Duplicates and blanks are based on existing CT DEEP protocols for other sampled nutrient parameters (i.e., at a rate of one per ten samples (10%)).

2.6 Lab Instrument/Equipment Testing, Inspection, and Maintenance (EPA QA/R-5 B6)

Preventative Maintenance

Preventative maintenance for all equipment is performed as per manufacturer's instructions and recommended schedule/frequency of performance in order to maintain equipment in good working condition and minimize downtime for all field and laboratory equipment. All preventative maintenance and repairs are performed either by qualified field or lab personnel or by the manufacturer's service engineers. An inventory of spare parts and consumables is maintained to an extent that is sufficient to maintain the operation of all equipment. Except for standard hardware, spare parts are obtained from the manufacturer or their representative or distributor.

Inspection

All equipment is inspected prior to each survey to assure it is in good working order. Any equipment found to be broken or malfunctioning is taken out of service and replaced as appropriate.

Table 2-6. Lab Equipment/Instrument Calibration, Maintenance, Testing and Inspection

Measurement	Instrument	Calibration	Maintenance	Frequency	Performance Requirements	Action items
Alkalinity	Metrohm 905 autotitrator ControsFIA TA Analyser	Performance verification and calibration with certified reference materials	Clean with fresh water daily following analysis run, as specified by manufacturer	Prior to analysis, between regular intervals during run (every 5 to 6 samples) and post analysis	See instrument technical specifications (Table 1-8 and 1-4)	Send to manufacturer if not calibrating
DIC	Apollo DIC analyzer				See instrument technical specifications (Table 1-7)	Send to manufacturer if not calibrating
pH	Agilent Cary 60 UV-Vis systems spectrophotometer				See instrument technical specifications (Table 1-5)	Send to manufacturer if not calibrating

2.7 Instrument/Equipment Calibration and Frequency (EPA QA/R-5 B7)

Lab Instrument calibration and frequency are summarized in Table 2-6. All laboratory instrument usage, maintenance, calibration, troubleshooting and service are performed according to the procedures documented in the manufacturer's operating manuals. All chemicals are obtained from the instrument

manufacturer or from vendors of scientific supplies. Individual instrument logbooks are used to record all maintenance and calibration activities.

Field equipment (YSI) is calibrated prior to each survey, according to manufacture instructions and CT DEEP SOPs, by Ms. O'Brien-Clayton or other permanent, trained CT DEEP staff. See LIS WQMP QAPP (CTDEEP, 2022) for details. Records of pre-survey, post-survey, and field calibrations will be kept with the calibration logs. Manufacturer calibration certificates are also kept with the calibration logs.

All laboratory analytical methods will undergo standardization prior to each analysis with the appropriate calibration standards that range beyond the expected field concentrations. Check standards and blanks will be run after every 4 to 6 samples depending on the analysis. All calibrations and blanks will be stored with the sample data both on the dedicated instrument computer and on the PI's computers. Metadata will be stored in the UCONN repository.

2.8 Inspection/Acceptance Requirements for Supplies and Consumables (EPA QA/R-5 B8)

All supplies and consumables will be inspected and accepted by the PIs and the graduate researchers prior to use on the project. Purchasing records are maintained within the UCONN and CT DEEP purchasing system. Supplies and consumables can be purchased only from state-approved vendors.

2.9 Data Acquisition Requirements (Non-Direct Measurements) (EPA QA/R-5 B9)

This project will make use of existing data collected by the [LIS RESPIRE and ALISE Projects](#). This dataset is of acceptable quality for this project because it has been collected under an EPA QAPP (RFA Number LI-00A00168) with the same measurement precision and accuracy goals as the current project. These data will be utilized as baseline conditions and provide an expected range for data collected under this project.

2.10 Data Management (EPA QA/R-5 B10)

Documentation for field surveys, laboratory analysis, and project finds is described in Section 1.9. Project data will be stored as ASCII plain text files, Microsoft Excel Worksheets, and Matlab binary data files in separate folders for each instrument type and laboratory analysis method. Scientific analysis of these data will be accomplished using Microsoft Excel and Matlab.

Data will be sent from the Vlahos lab to CT DEEP electronically as Microsoft Excel Worksheets on a template specified by CT DEEP. CT DEEP will store the project data in an Access database and/or SQL database and uploaded to WQX to be made publicly available through the Water Quality Data Portal. CT DEEP databases are housed on state servers and backed up nightly. The CT DEEP database is also uploaded to the UCONN ERDDAP bi-weekly during the summer months of June-September and annually in December.

Data will be uploaded to AWX by CT DEEP upon receipt from the analytical lab. As data will be received from the lab in Excel spreadsheets formatted to CT DEEP specifications, no data processing or manipulation will be performed. Data from AWX are uploaded to WQX monthly.

3.0 ASSESSMENT AND OVERSIGHT

3.1 Assessments/Oversight and Response Actions (EPA QA/R-5 C1)

The project schedule (Table 1-1) guides the progress of this project. PIs will quality check all project results and verify that correct analysis methods are applied within two months of field surveys and one month of laboratory analysis. Post-processing scientific analysis will be quality checked upon or prior to presentation. Data quality issues will be dealt with by flagging or rejecting data, checking instrument calibration and functioning, and re-running laboratory analysis when possible. Quality assessment and oversight as well as any response actions taken will be detailed in the project reports described below.

3.2 Reports to Management (EPA QA/R-5 C2).

Progress reporting of overall project activities will be submitted as part of CTDEEP's LISS Semi-annual Performance Reports to EPA, and other LISS reporting by the CTDEEP LISS Coordinator, or as requested by EPA Project Officer. In future years, a summary final report of activities and major findings and a listing of data products will be submitted by the Vlahos lab to DEEP annually following completion of monitoring and analysis activities. Requests and notifications of major changes or issues will be communicated with project management as necessary.

4.0 DATA REVIEW AND USABILITY

4.1 Data Review, Verification, and Validation Requirements (EPA QA/R-5 D1)

It is anticipated that majority of data collected will be useful to support the scientific objectives. However, review, verification, and validation of the data collected in the field and the results of laboratory analysis are necessary. The data recorded by field instrumentation need to be checked against field logs for time and position consistency. The field data also need to be checked for measurements that should not be included in analysis, unphysical outliers that are above reasonable upper bounds or below reasonable lower bounds, and data spikes (statistical outliers) that may unduly influence subsequent averages. Results from laboratory analysis will be checked against blank samples and replicate results to verify the results are above analytical background noise and assess the statistical uncertainty of reported values.

4.2 Verification and Validation Methods (EPA QA/R-5 D2)

The consistent application of methods provided in the DEEP SOPs and QAPP provide good certainty that the data are both valid and usable. Any missing samples will be reported to record completeness and results will be further reviewed to be sure they are consistent with expected parameter ranges in Long Island Sound. Data outside expected ranges or inconsistent with SOPs or the QAPPs will be flagged in the database.

Laboratory analytical methods incorporate checks on data quality. Blanks are run to determine instrument response without real signal. Sample concentrations must return larger instrument response than blanks to be included in further analysis. Concentrations from replicates will be compared to calculate the replicate data range for each time, depth, and station. The replicate data range will be compared to the standard deviation of all samples for each survey. Where the replicate data range is larger than the survey standard deviation, the concentration will be flagged due to inconsistent replicates. The replicate data range for each location will be reported as an estimate of measurement uncertainty.

4.3 Reconciliation with User Requirements (EPA QA/R-5 D3)

Data from each survey will be reviewed by the PIs for compliance with the QAPP, correctness, and consistency. Results that do not pass the verification and validation checks described above will be flagged along with the reason for data rejection. Data flags will be included in the project database. Usable results will be included in scientific analysis and will be described in project reports.

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APPENDICES

Appendix A OA Sample Field Collection SOP

Vlahos Lab Field Sampling SOPs

Lauren Barrett

Updated 2023/02/01

TA, DIC, and pH samples will be processed from one sample container now:

Materials: 250mL borosilicate bottles, Apiezon grease, hose clamps, rubber bands, saturated mercuric chloride

- Samples should be taken with gas-sensitive considerations
- Attach 0.2 um reusable Whatman Polycap TC (polyethersulfone) inline filter to the Niskin bottle tubing. Allow sample water to run through the filter and the tubing to flush.
- Rinse sample containers and caps three times with ~50 mL sample water.
- Insert sample tubing to the bottom of the sample bottle. Tip upside down to rinse out the container with sample water for a few seconds. Then return upright and fill from the bottom with at least two overflows. Keep the water flowing, raise the sample tubing to near the shoulder of the vial, then crimp the tubing to stop flow, leaving ~1% headspace (a few mL) in the bottle.
- Place the sample bottle in the mercuric chloride secondary containment. Utilizing the designated pipette provided by the Vlahos lab, fitted with a new, clean tip, add 100 uL of saturated mercuric chloride solution to the bottle being careful not to introduce air into the sample.

****CAUTION****

Mercuric chloride is toxic. Be sure to wear nitrile gloves and always store in secondary containment. If spilled rinse thoroughly with water. MSDS is available upon request.

- Put three vertical stripes of Apiezon grease on the ground glass stopper. Push the stopper straight into the bottle and turn to coat the neck with grease.



- Secure a rubber band around the top of the ground glass stopper using a hose clamp. I recommend putting the band around the hose clamp first (see image below), then stretching the band over the stopper and securing the hose clamp around the neck.



- Place the sample in the provided sample box so it is secured by surrounding foam.

Place the vial into a zip top bag with bubble wrap and place the bag into the cooler.

At the end of the day's sampling, rinse the filter by running Deionized water through it in both directions.

Appendix B- Sample Chain of Custody

FIELD SAMPLES/DELIVERY RECORD

COASTAL ACIDIFICATION ANALYSES

Sample Source: Long Island Sound	FROM: Katie O'Brien-Clayton LIS WQMP, BWPLR CTDEEP 79 Elm St. Hartford, CT 06106-5127 (860) 424-3176 FAX 424-4055
Sample Collector:	
Project: LISB	
Job:	
SDG:	

Date of Delivery:

LIM Number	Sample Code	DIC	pH	TA	TA Filtered	Date of Collection	Salinity (PSU)	Temperature (°C)	Preserved with HgCL Y/N
	A4S	40	40	500	500				
	A4S Dup	40	40	500	500				
	A4B	40	40	500	500				
	C1S	40	40	500	500				
	C1B	40	40	500	500				
	D3S	40	40	500	500				
	D3B	40	40	500	500				
	E1S	40	40	500	500				
	E1B	40	40	500	500				
	O9S	40	40	500	500				
	O9B	40	40	500	500				
	I5S	40	40	500	500				
	I5B	40	40	500	500				
	F2S	40	40	500	500				
	F2B	40	40	500	500				
	H4S	40	40	500	500				
	H4B	40	40	500	500				
	I2S	40	40	500	500				
	I2B	40	40	500	500				
	K2S	40	40	500	500				
	K2B	40	40	500	500				
	Blank	40	40	500	500				

Test Variables:

RELINQUISHED BY: (SIGNATURE)	Date & Time	RECEIVED BY: (SIGNATURE)	Date & Time

Signature: *Mary E Becker*
 Email: Mary.Becker@ct.gov










QAPP CTDEEP LIS _OA Monitoring_for signatures_4.4.23















Final Audit Report

2023-05-04

Created:	2023-04-04
By:	Katie O'Brien-Clayton (katie.obrien-clayton@ct.gov)
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-  Document created by Katie O'Brien-Clayton (katie.obrien-clayton@ct.gov)
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-  Signer Katie O'Brien-Clayton (katie.obrien-clayton@ct.gov) entered name at signing as Katie O'Brien-Clayton
2023-04-04 - 3:43:12 PM GMT- IP address: 159.247.3.230
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Signature Date: 2023-04-04 - 3:43:14 PM GMT - Time Source: server- IP address: 159.247.3.230
-  Document emailed to matthew.lyman@ct.gov for signature
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-  Signer matthew.lyman@ct.gov entered name at signing as Matthew Lyman
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-  Document e-signed by Matthew Lyman (matthew.lyman@ct.gov)
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-  Document e-signed by Mary Becker (Mary.Becker@ct.gov)
Signature Date: 2023-04-13 - 12:28:36 PM GMT - Time Source: server- IP address: 73.182.178.243
-  Document emailed to Penny Vlahos (penny.vlahos@uconn.edu) for signature
2023-04-13 - 12:28:39 PM GMT
-  Email viewed by Penny Vlahos (penny.vlahos@uconn.edu)
2023-04-17 - 7:36:18 PM GMT- IP address: 104.47.70.126
-  Email viewed by Penny Vlahos (penny.vlahos@uconn.edu)
2023-05-03 - 3:49:35 PM GMT- IP address: 104.47.55.126
-  Document e-signed by Penny Vlahos (penny.vlahos@uconn.edu)
Signature Date: 2023-05-03 - 3:58:49 PM GMT - Time Source: server- IP address: 137.99.198.154
-  Document emailed to mcnally.elise@epa.gov for signature
2023-05-03 - 3:58:52 PM GMT
-  Email viewed by mcnally.elise@epa.gov
2023-05-03 - 4:43:49 PM GMT- IP address: 104.47.64.254
-  Signer mcnally.elise@epa.gov entered name at signing as Elise McNally
2023-05-03 - 6:31:36 PM GMT- IP address: 204.46.78.212
-  Document e-signed by Elise McNally (mcnally.elise@epa.gov)
Signature Date: 2023-05-03 - 6:31:38 PM GMT - Time Source: server- IP address: 204.46.78.212
-  Document emailed to spencer.evelyn@epa.gov for signature
2023-05-03 - 6:31:40 PM GMT
-  Email viewed by spencer.evelyn@epa.gov
2023-05-04 - 3:05:25 PM GMT- IP address: 104.47.64.254
-  Signer spencer.evelyn@epa.gov entered name at signing as Evelyn Spencer
2023-05-04 - 3:07:21 PM GMT- IP address: 134.67.29.82
-  Document e-signed by Evelyn Spencer (spencer.evelyn@epa.gov)
Signature Date: 2023-05-04 - 3:07:23 PM GMT - Time Source: server- IP address: 134.67.29.82
-  Agreement completed.
2023-05-04 - 3:07:23 PM GMT