

QUALITY ASSURANCE PROJECT PLAN

LONG ISLAND SOUND AMBIENT WATER QUALITY MONITORING PROGRAM

2017

STATE OF CONNECTICUT
DEPARTMENT OF ENERGY & ENVIRONMENTAL PROTECTION
BUREAU OF WATER PROTECTION AND LAND REUSE
(formerly the Department of Environmental Protection/Bureau of Water Management)
79 Elm Street
Hartford, Connecticut 06106-5127

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A PROJECT MANAGEMENT

A1 TITLE AND APPROVALS:

TITLE: CTDEEP Long Island Sound Ambient Water Quality Monitoring Program Quality Assurance Project Plan, May 2017

Connecticut Department of Energy & Environmental Protection (CTDEEP)
Bureau of Water Protection and Land Reuse (BWPLR)
Water Planning & Management Division/Water Planning
Water Monitoring/Long Island Sound Ambient Water Quality Monitoring Program
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A4 Project Organization

Refer to Figure A4-1, Project Organization. Leah O'Neill, EPA New England, will have administrative oversight of the project. The project is planned, organized, and implemented by the Connecticut Department of Energy & Environmental Protection, Bureau of Water Protection and Land Reuse, Water Planning & Management Division. The Supervisor of the Division's Long Island Sound Monitoring group (currently Christopher Bellucci) will be responsible for overall program supervision. Current staff Christine Olsen, Environmental Analyst 3 in the Long Island Sound Monitoring group, will be responsible for QA review, conducting appropriate reviews of laboratory data, laboratory QC, ensuring that QA and reporting requirements are met, review and verification of data, including quality assurance data, for completeness and to document any obvious or suspected problems; accuracy and completeness of the Program database; and coordination with laboratory QA manager to rectify any obvious or suspected problems. Current staff Matthew Lyman, Environmental Analyst 3 in the Long Island Sound Monitoring group, will be responsible for oversight of all field operations and data management of the monitoring program, including: scheduling and logistics; hiring and training seasonal assistants; overseeing and directing activities of field/office program staff; ensuring that field staff have reviewed Program QAPP and SOPs, received appropriate training in field and data entry/processing methods, and have shown competence in the performance of assigned duties; field data and sample chain-of-custody documentation; and database development and maintenance. Current staff Katie O'Brien-Clayton, Environmental Analyst 2 in the Long Island Sound Monitoring group, will be responsible for documentation, records, and reporting and assisting with field operations logistics including scheduling and conducting field surveys, hiring and training of seasonal field staff, and data entry and processing.

The University of Connecticut Center for Environmental Science and Engineering (CESE), Analytical Services/Nutrients Lab, or other capable laboratory will provide nutrient analytical services. The Laboratory's Director and/or Quality Assurance Officer will direct and ensure quality for the laboratory procedures. The Laboratory's Nutrient Lab Chemist or Technician will be responsible for nutrient lab sample handling and custody procedures and sample analyses as well as the provision of required supplies to the field crew.

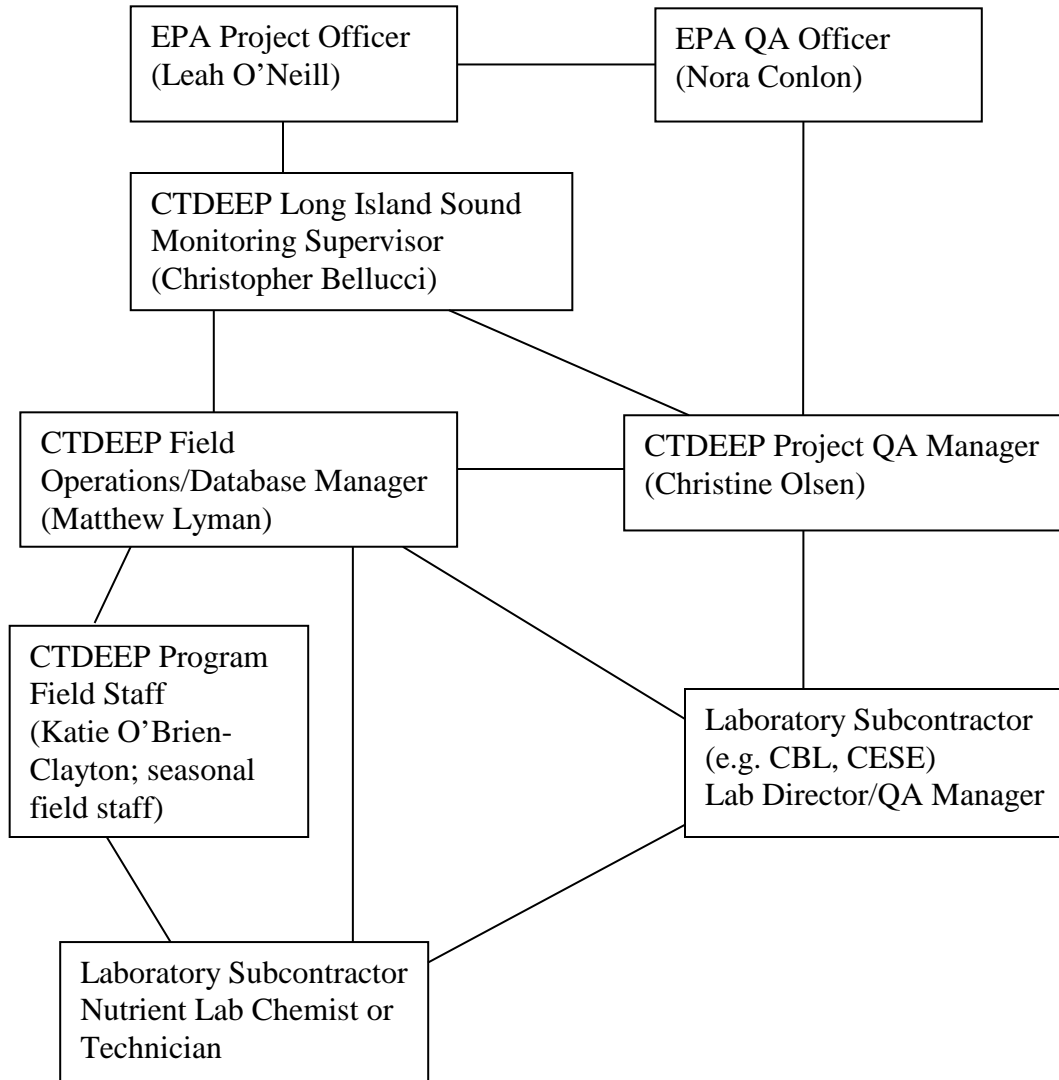


Figure A4-1. Project Organization.

A5 PROBLEM DEFINITION/BACKGROUND

A5.1 Purpose/Background

To complement the development of a coupled hydrodynamic-water quality model being prepared as part of the Long Island Sound Estuarine Study (LISS) by the National Oceanic and Atmospheric Administration (NOAA) and Hydroqual, Inc., a series of comprehensive field surveys were conducted during 1988, 1989 and 1990. These surveys, designed to provide water column data essential to initialize, calibrate, and verify the numerical models, were conducted by the Marine Sciences Institute (MSI) of the University of Connecticut, the Marine Sciences Research Center (MSRC) of the State University of New York at Stony Brook, and the New York City Department of Environmental Protection (NYCDEP). The range of effort included in this work served to significantly extend the database developed over the preceding two years of the program, detailing water temperature- salinity structure throughout the Sound and established the first comprehensive dataset providing reasonably synoptic observations of flow and concurrent water quality characteristics on a Sound-wide basis. Such a data set was considered essential to modeling efforts and thus to management strategy development and implementation.

In an effort to provide continuity to the dataset developed during the years since the LISS Program was initiated, and to provide continuity from the research/evaluation phase of the program into the implementation phase, the CT DEEP (formerly DEP) initiated a Long Island Sound Ambient Water Quality Monitoring Program in January of 1991. This Program has continued, with EPA support, and has been expanded from 7 stations sampled monthly (January 1991 through December 1994) to 17 stations sampled monthly (April 2002 to present), with a period during which 18 stations were sampled monthly (January 1995 to March 2002). A Summer Hypoxia Survey, focused on observations of the area and duration of hypoxia in the bottom waters of the Sound each summer, samples up to thirty additional stations on a bimonthly basis through the summer months (mid-June through mid-September). These surveys monitor offshore waters of Long Island Sound only. Nearshore waters of less than 5-meter depth, and embayments are not part of the monitoring covered by this QAPP.

The LISS identified low dissolved oxygen (DO) in the bottom waters of the Sound as the highest priority issue and implemented a process to reduce nutrient loads to the Sound in an effort to improve bottom water DO conditions over time. The data to be provided by these surveys is considered essential to the continued evaluation of model predictions, and to monitor the effectiveness of management actions being taken to reduce nitrogen sources to the Sound.

The goals of the Department's Long Island Sound Ambient Water Quality Monitoring Program are:

- To monitor water quality parameters year round on a monthly schedule at stations throughout Long Island Sound
- To monitor the temporal and spatial extent of summertime hypoxia through Sound-wide sampling every other week from late June through mid-September

- To maintain a long-term database of the information collected

The objectives of the Program are:

- To review the data periodically, in combination with available historical data, for trends
- To assess the long-term results of specific management actions such as the “no-net increase” nutrient (nitrogen) policy adopted in 1990 and the nutrient reduction strategy implemented in 1994
- To provide state and federal managers and policy-makers with information on existing conditions and trends that can be used in the development, implementation and assessment of strategies to control and improve water quality in the Sound
- To make the data available for related efforts such as water quality assessments, research, TMDL development and evaluation, and water quality model development and calibration
- To make data available to other interested individuals/groups

A6 Project Description and Schedule

Schedule of Surveys

The Monthly Field Survey involves sampling at 17 fixed stations (Figure A6-1 and Table A6-1), each station sampled once per month, generally during the first week of the month, and year-round.

The Summer Hypoxia Survey typically involves sampling at a minimum of 20 stations, up to a maximum of 42 from 47 available (Figure and Table A6-1). Sampling is conducted every other week beginning the third week of June through the first week of September, for a total of six unique surveys. This survey is combined with the Monthly survey during the July, August, and September Monthly surveys, with the fixed Monthly stations contributing to the total number of stations sampled for purposes of assessing hypoxic conditions. Hypoxia is most prevalent in the western-to-central sound (the Narrows, Western Basin and the western half of the Central Basin), so stations in these areas will tend to be sampled with higher frequency. Dissolved oxygen observations of less than 3.5 mg/L during the early September (Monthly) survey will dictate the need for a seventh survey to be conducted on or about the third week of September. The first (mid-late June) and last (mid-late September, when conducted) Hypoxia surveys of each summer season may involve sampling at fewer than 20 stations since these surveys are often conducted when hypoxia is absent or involves only a relatively small spatial area, so that an assessment of the area affected can be accomplished with fewer samples.

Calendar, weather, vessel/crew availability, and competing project constraints are expected to

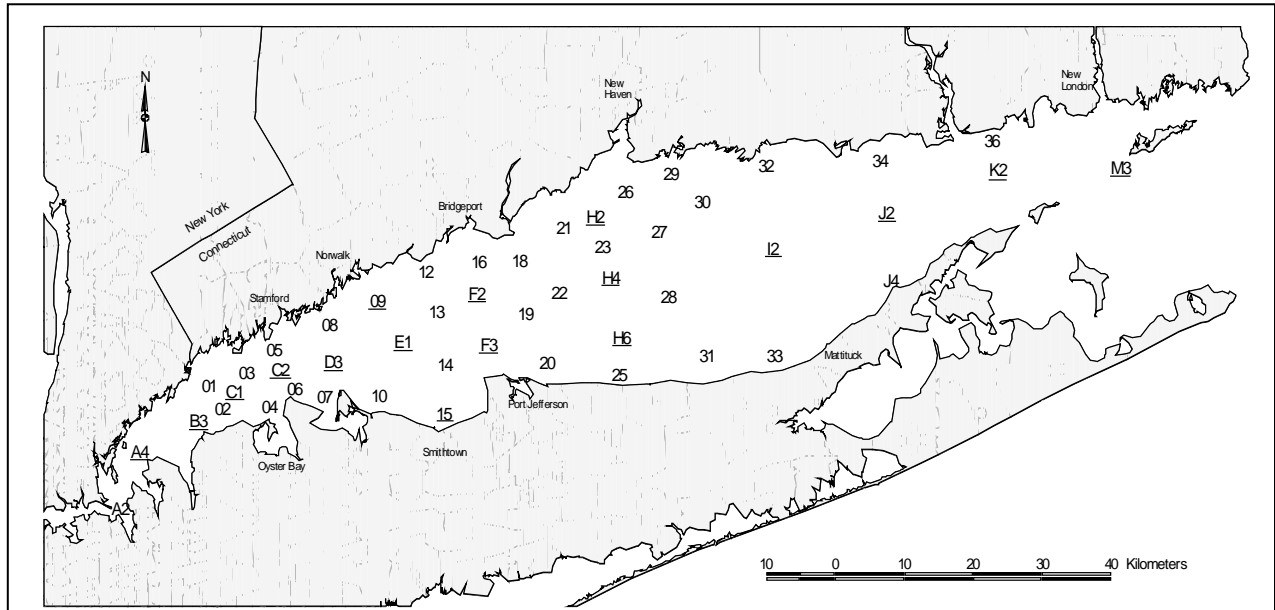


Figure A6-1. CTDEP Long Island Sound Ambient Water Quality Monitoring Program station map. Seventeen underlined stations serve as monthly water quality monitoring sites. Thirty additional sites are sampled, at varying frequencies, during summer hypoxia surveys. See Table A6-1 for station information.

occasionally affect this schedule, resulting in samples taken earlier or later, or occasional missed samples.

Parameters

Parameters and methods utilized during the previous twenty-six years of the Long Island Sound Water Quality Monitoring Program will be continued (Table A7-1 and Table A7-2). Field sampling will be conducted by personnel from CTDEEP. Filtration of samples for nutrient analyses will be conducted in the field and all filters and filtrate samples prepared will be delivered to an appropriate laboratory, with proven capability with regard to low-level estuarine nutrient analysis. Laboratories that have provided analytical services in the past, and are most likely to be used going forward include the Nutrient Analytical Services Laboratory of the University of Maryland, Center for Environmental Science, Chesapeake Biological Laboratory (NASL-CBL); and the University of Connecticut's Center for Environmental Sciences and Engineering (UConn-CESE). Field methods, apparatus, sample types and sample handling information are contained in Tables B2-1, B3-1, and B4-1.

Data Availability

All field data, including the CTD profile data will be processed within one month of recovery, and

then available in the Program's database. Analytical data from the contract laboratory will be available in the Program's database as soon as practical, following receipt and review. Laboratory data and QC reports are expected within 60 days of sample delivery.

Summary reports will be prepared following each Summer Hypoxia survey and submitted to EPA and other interested parties via email, typically within one week of the survey completion. Annual Hypoxia Survey reports, including a summary of the year's hypoxic event and comparisons to previous years will be submitted to EPA within six months of the Survey end. Progress reports of the Monthly Survey can be prepared for submission to EPA upon request of the Project Officer.

Table A6-1. Station information. See Figure A6-1.

Station Name	Station Depth (meters)	Latitude	Longitude	General Schedule	Sampling Record	Notes
Narrows						
A4	32.6	40 52.35N	73 44.05W	Year round	8/94 - present	
B3	18.0	40 55.10N	73 38.57W	Year round	2/91 - present	
01	14.8	40 57.80N	73 37.42W	Summer	6/94 - present	
02	15.8	40 56.08N	73 36.04W	Summer	6/94 - present	
C1	19.8	40 57.35N	73 34.82W	Year round	12/94 - present	
03	24.1	40 58.76N	73 33.64W	Summer	6/94 - present	
04	12.3	40 56.27N	73 31.16W	Summer	6/94 - present	
C2	32.4	40 59.06N	73 30.13W	Year round	12/94 - present	
05	13.0	41 00.56N	73 30.82W	Summer	6/94 - present	
06	18.2	40 57.67N	73 28.60W	Summer	6/94 - present	
07	12.7	40 57.02N	73 25.52W	Summer	6/94 - present	
08	12.9	41 02.45N	73 25.08W	Summer	6/94 - present	
D3	40.9	40 59.63N	73 24.68W	Year round	2/91 - present	
Western Basin						
09	9.1	41 04.25N	73 20.17W	Year round	6/94 - present	
10	17.3	40 57.10N	73 19.95W	Summer	6/94 - present	
E1	38.1	41 01.16N	73 17.48W	Year round	12/94 - present	
12	10.5	41 06.52N	73 15.18W	Summer	6/94 - present	
13	22.3	41 03.50N	73 14.06W	Summer	6/94 - present	
14	25.4	40 59.49N	73 13.13W	Summer	6/94 - present	
15	15.3	40 55.88N	73 13.27W	Year round	6/94 - present	
16	8.9	41 07.22N	73 09.75W	Summer	6/94 - present	
F2	19.7	41 04.82N	73 09.92W	Year round	12/94 - present	
F3	40.9	41 01.07N	73 08.67W	Year round	1/91 - present	
Central Basin						
18	12.6	41 07.34N	73 05.40W	Summer	6/94 - present	
19	25.5	41 03.32N	73 04.85W	Summer	6/94 - present	
20	22.5	40 59.64N	73 02.54W	Summer	6/94 - present	
21	14.3	41 09.84N	73 00.89W	Summer	6/94 - present	
22	26.9	41 04.94N	73 01.37W	Summer	6/94 - present	
H2	13.9	41 10.68N	72 57.63W	Year round	6/94 - present	
23	19.0	41 08.41N	72 56.93W	Summer	6/94 - present	
H4	23.7	41 06.10N	72 56.04W	Year round	6/94 - present	
H6	41.4	41 01.56N	72 54.81W	Year round	1/91 - present	
25	10.7	40 58.86N	72 55.09W	Summer	6/94 - present	
26	11.2	41 12.55N	72 54.51W	Summer	6/94 - present	
27	20.2	41 09.52N	72 50.97W	Summer	6/94 - present	
28	30.1	41 04.69N	72 50.01W	Summer	6/94 - present	
29	9.4	41 13.89N	72 49.78W	Summer	6/94 - present	
30	15.3	41 11.78N	72 46.52W	Summer	6/94 - present	
31	25.8	41 00.25N	72 46.10W	Summer	6/94 - present	sampled infrequently
32	10.7	41 14.49N	72 39.94W	Summer	7/94 - present	sampled infrequently
I2	27.3	41 08.25N	72 39.30W	Year round	1/91 - present	
Eastern Basin						
33	20.2	41 00.23N	72 39.07W	Summer	6/94 - present	sampled infrequently
34	16.7	41 14.76N	72 28.10W	Summer	6/94 - present	sampled infrequently
J2	21.8	41 10.92N	72 27.46W	Year round	6/94 - present	
J4	18.5	41 05.85N	72 27.00W	Summer	6/98 - present	sampled infrequently
36	6.6	41 16.23N	72 16.53W	Summer	7/94 - present	sampled infrequently
K2	37.7	41 14.06N	72 15.95W	Year round	7/94 - present	
M3	72.6	41 14.23N	72 03.20W	Year round	1/91 - present	

A7 Quality Objectives and Criteria

The primary focus of the CTDEEP's Long Island Sound Ambient Water Quality Monitoring Program is to monitor and document basic water column characteristics (temperature, salinity, density, light, chlorophyll, suspended solids) and nutrient concentrations to detect changes over time and be able to estimate the rate of any such changes. The Program also serves as a long-term, consistent data source to support Long Island Sound related research. Because the Program's focus is measurements, goals for data quality focus on individual measurements. With regard to long-term trend analyses, the data quality objective is that for each variable of interest (ambient nitrogen, phosphorus, chlorophyll *a*, dissolved oxygen, etc.) an existing trend can be detected with 95% confidence, and the rate of change estimated within 20%.

Measurement Quality Objectives

One measure of data quality is completeness. With regard to analytical laboratory measurements the goal for record completeness is 100%. Twenty-six years of sampling on this monitoring program (January 1991 through December 2016) has produced a dataset with a 96% completeness record with regard to expected station visits. During the most recent five-year period, 2012-2016, 100% of expected stations visits were completed. If missed station visits are not considered, the completeness of the analytical data through November 2016 (for all completed station visits) is 99%. For some years, 100% completeness in both areas was achieved. 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.

With regard to Water column profile data obtained with a Conductivity-Temperature-Depth (CTD) profiler, the achievable level of data completeness is somewhat less, but still very high overall. Over the first nineteen years of data (through May 2010), the total number of CTD-related records was over 680,000 (including all survey types) [511,000 from monthly WQ surveys only] compared with 103,800 [101,900 from monthly WQ surveys only] nutrient/analytical records. Each CTD record holds data averaged from a 0.2 meter slice of the water column. A single profile from a 20 meter deep station, for example, would be expected to have approximately 100 records. Overall, nineteen years of sampling produced a CTD dataset better than 96% complete, based on existing profiles. In addition, there are profiles that were never obtained because of missed station visits, inoperable or malfunctioning equipment, or operator error. Because the dissolved oxygen sensor is a separate component and is affected by clogged plumbing and membrane problems, dissolved oxygen data may be lost without the concurrent loss of pressure, temperature and salinity data within that depth record. In fact, a review of the CTD data (nineteen years, through May 2010) shows dissolved oxygen data is incomplete approximately 5% of the time, compared to available CTD pressure data. Comparatively, CTD-measured temperature is incomplete 2% of the time, and conductivity/salinity 3% of the time.

A second measure of data quality is representativeness. Sampling occurs monthly, year-round at

fixed station locations. 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. Sample collection and handling procedures are important to maintain representativeness, and they must be followed consistently. Samples stored temporarily in Niskin sample collection bottles must be well-mixed before any subsample is drawn. Samples must be stored according to SOP specifications to maintain sample integrity until analysis.

A third measure of data quality is comparability. Program sampling procedures are based on previous data collection efforts of the Long Island Sound Study and were designed in concert with participants from this previous monitoring, water quality model development team, and expert participants in the development of the LISS Monitoring Plan to support the CCMP. Most sampling and analytical procedures remain the same as those implemented over the previous nineteen years of this monitoring program. Consistent field and laboratory procedures, well-documented by the appropriate SOPs, help ensure consistent and reproducible data. Changes in methods will be accompanied by a period of split samples, allowing for adequate comparison between the results of the new method and the old. Beginning in 2010 the analytical laboratory being used for sample analysis has been required to participate in a multi-lab comparison program that provides data specifically to assess the laboratory's ability to produce data comparable to several other laboratories located in the Northeast and Mid-Atlantic regions of the United States (see further discussion below).

Procedures for Assessing Accuracy and Precision:

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; the analysis of matrix spikes, replicates, and blanks). The 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 (Appendix B). A number of routine quality control (QC) 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. The Continuing Calibration Verification (CCV), by analysis of standard reference materials (including, when available, EPA

Quality Control Solutions) must fall within the control limits of 85-115% of the true value for instrument performance to be deemed acceptable.

Beginning in 2010, the laboratory providing nutrient analytical services was and will continue to be required to participate in the Chesapeake Bay Blind Audit Program. The current program provides estuarine nutrient samples to laboratories twice per year for interlab comparisons of analytical results. Samples include both particulate and dissolved (high and low concentrations) samples for all of the standard analytes (carbon, nitrogen, phosphorus), plus chlorophyll. Typically twelve, or more, laboratories participate. The comparison data is valuable as an ongoing evaluation of laboratory accuracy in methods and results. The CTDEEP made participation in this semi-annual audit a condition of the scope-of-work agreement with UCONN-CESE, and will continue to require participation by any primary lab services provider as long as the program is available. The audit program is administered by NASL-CBL of the University of Maryland, which is also a participating laboratory.

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.

Accuracy and precision goals for measured parameters are provided in Tables A7-1 and A7-2, 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.

Table A7-1. Measurement quality objectives and quality assurance sample information for field water column observations.

Variable	Precision Goal	QA Sample Type	Frequency of QA	Data Generated
Depth	± 0.5 m	Performance verification at certified calibration facility	Annually	CTD response vs. calibration standards; annual drift
Depth	± 0.5 m	QC check against vessel's depth finder	Every cast	Difference between CTD station depth and on-board depth finder
Temperature	± 0.5 °C	Performance verification at certified calibration facility	Annually	CTD response vs. calibration standards; annual drift
Temperature	± 0.5 °C	QC check against secondary thermistor in DO sensor module	Every cast	CTD temperature vs. oxygen sensor temp
Salinity	± 0.5 psu	Performance verification at certified calibration facility	Annually	CTD response vs. calibration standards; annual drift

Table A7-2. Measurement quality objectives and quality assurance sample information for laboratory analyses.

Variable	Accuracy Goal	Precision Goal	QA Sample Type	Frequency of QA	Data Generated
Analytical Laboratory Measurements					
Ammonia (NH₃)	85-115%	15%	Standards, spikes, lab and field duplicates; semiannual audit	Per batch; one cruise	Relative accuracy and precision
Nitrate + Nitrite (NO₃⁻+NO₂)	85-115%	15%	Standards, spikes, lab and field duplicates; QC check against Day-0 whole water BOD sample at up to 10 stations; semiannual audit	Per batch; one cruise	Relative accuracy and precision; secondary NO _x measurement on fresh sample
Total Dissolved Nitrogen (TDN)	85-115%	15%	Standards, spikes, lab and field duplicates; semiannual audit	Per batch; one cruise	Relative accuracy and precision
Particulate Nitrogen (PN)	85-115%	15%	Field blanks and field duplicates; semiannual audit	Per batch; one cruise	Precision; estimate of field contamination
Orthophosphate (PO₄³⁻) or (DIP)	85-115%	15%	Standards, spikes, lab and field duplicates; semiannual audit	Per batch; one cruise	Relative accuracy and precision
Total Dissolved Phosphorus (TDP)	85-115%	15%	Standards, spikes, lab and field duplicates; semiannual audit	Per batch; one cruise	Relative accuracy and precision
Particulate Phosphorus (PP)	85-115%	15%	Standards, spikes, field blanks, lab and field duplicates; semiannual audit	Per batch; one cruise	Relative accuracy and precision; estimate of field contamination
Dissolved Organic Carbon (DOC)	85-115%	15%	Standards, spikes, lab and field duplicates; semiannual audit	Per batch; one cruise	Relative accuracy and precision
Particulate Carbon (PC)	85-115%	15%	Field blanks and field duplicates; semiannual audit	Per batch; one cruise	Precision; estimate of field contamination
Dissolved Silica (SiO₂)	85-115%	15%	Standards, spikes, lab and field duplicates	Per batch; one cruise	Relative accuracy and precision
Biogenic Silica (BioSi)	85-115%	15%	Standards, spikes, field blanks, lab and field duplicates	Per batch; one cruise	Relative accuracy and precision; estimate of field contamination
Chlorophyll <i>a</i> (Chl a)	85-115%	15%	Standards, spikes, field blanks, field duplicates; semiannual audit	Per batch; one cruise	Relative accuracy and precision; estimate of field contamination
Total Suspended Solids (TSS)	NA	15%	Standards, field blanks and duplicates; replicates averaged	Per batch; one cruise	Precision; estimate of field contamination
Biological Oxygen Demand (BOD)	NA	15%	Field duplicate	Per batch; one cruise	Precision

Table A7-3. Manufacturer's equipment specifications.

SPECIFICATIONS: SBE-19 SeaCat Profiler (from: *SeaBird Electronics, Inc.*)

Measurement Range:

Temperature -5 to +35 °C
 Conductivity 0 to 7 S/m (0 to 70 mmho/cm)
 Pressure *Strain Gauge Sensor* 150 psia

Accuracy:

Temperature 0.01 °C/6 months
 Conductivity 0.001 S/m/month
 Pressure *Strain Gauge Sensor* 0.25% of full scale range (150 psia)

Resolution:

Temperature 0.001 °C
 Conductivity 0.0001 S/m
 Pressure *Strain Gauge Sensor* 0.015% of full scale range (150 psia)

Sensor Calibration:

Temperature -1 to +31 °C
 Conductivity 0 to 7 S/m. Physical calibration over the range 1.4 - 6 S/m.
 Pressure 0 to full scale in 20% steps

SPECIFICATIONS: SBE-23 Dissolved Oxygen Sensor (from: *SeaBird Electronics, Inc.*)

Type: Modified YSI Model 5739 oxygen probe
 Temp. Range: -5 to +45 °C
 Thermistor Accuracy: 0.2 °C
 Response Time: two seconds

SPECIFICATIONS: WETStar Fluorometer (from: *WetLabs, Inc.*)

Rated Depth: 600 meters
 Response Time: 0.17 sec
 Optical Sensitivity: 0.03 µg/l
 Dynamic Range: 0.03–75 µg/l

SPECIFICATIONS: LI-193SA Spherical Quantum Sensor (from: *LI-COR, Inc.*)

Rated Depth: 350 meters (500psi)
 Detector Type: Silicon photovoltaic
 Sensitivity: 7µA per 1000µmols/sec/m²
 Stability: < 2% change over one year
 Angular Response: < 4% error up to 90° from normal axis (top half of sphere)
 Abs. Calibration: Within 5% in air
 Response Time: 10 µS

A8 Special Training Requirements/Certification

Any CTDEEP staff member who participates in field operations will be trained, as needed, in each field function they will be required to perform (equipment handling, filtering tasks, titrations, etc.) and their performance closely observed. Training will be conducted by the technical project supervisor, the field operations manager, or their designee. All procedures for equipment handling, sample collections, and sample handling, including procedures for Winkler titrations and filtering are documented in the *Long Island Sound Ambient Water Quality Monitoring Program Water Quality and Hydrographic Surveys Standard Operating Procedures Manual, 2017 (SOP) (Appendix A)*. All personnel that will assist with this monitoring will be required to review the SOP prior to participating in a survey, and all personnel will be supervised, at a minimum, the first two times any new task is performed. Staff will not be allowed to proceed unsupervised unless and until they have shown proficiency in each particular field activity. Proficiency will be based on the individual's ability to progress through each documented step of a procedure with no reminders and no errors in method. Of particular importance in field sample handling is avoiding sample contamination, maintaining well-mixed samples, accurate volume measurements, and accurate data recording. At least one permanent staff of the Program will be present on the vessel during field operations, so that new staff performance will continue to be evaluated. At least two fully trained staff will be present whenever staff-in-training are onboard the research vessel.

A9 Documentation and Records

Field Activities

Field crews will record appropriate data on hardcopy field datasheets (Appendix A). All of the information contained on the Field Datasheet will be entered into the Program's database with the use of an electronic Field Datasheet Form, designed to resemble the hardcopy form. All field data will be entered into the electronic database form within one week of the end of each survey. This database form is designed with protections against incorrect entries (e.g. it will not allow duplicate station entries) and all field datasheets entries will be performed twice. A program to compare the two unique entries will then be used to find any typographic errors. Once any errors are corrected, the field data will be uploaded to the appropriate database table. This dual entry virtually eliminates the chances of typographical errors since any item that does not match between the two entries will be verified using the field datasheet. Limits will be placed on some of the entry fields as well (e.g. if air temperature entry falls outside the range [-10 - +35°C] text will appear: [temperature is not within reasonable range]). All latitude/longitude coordinates entered will be mapped to confirm they are within the expected area. Outliers are generally easy to pick out, for example when a 73° longitude is recorded instead of a 72, or vice versa.

The CTD profiler will generally be operated in real-time, allowing real-time capture of the data file in electronic form. When the CTD is not being operated in real-time, data files will be uploaded to the computer as soon as possible in the field to confirm that a complete file was obtained. CTD files are named with the station name and date for easy identification later. CTD data files are reviewed and processed prior to upload to the Access database. Original, raw and processed CTD files are maintained for archival once the final processed files are uploaded to the Program database.

A Data File Processing Record (Appendix A) is used to document the status of processing for each CTD file from any particular cruise. A Data Processing Cover Sheet (Appendix A) is used to document the status of all field data entry and CTD file processing for a particular cruise. These two documents are filed with the original Field Datasheets, by cruise and year. Current procedure calls for maintenance of these paper files in full. Field Datasheets are also scanned and maintained in electronic format.

The Program database links all station/date specific data. All CTD profile data records are uniquely identified by the Station Name, Cruise Name, and depthx10. All nutrient data are uniquely identified by the Station Name, Cruise Name, DepthCode (S, B, etc), and parameter.

Sample Custody Procedures

Sample labeling and custody procedures are discussed in Section B3, Sample Handling and Custody. Appropriate chain of custody paperwork will accompany all samples from collection to the analytical facility (Appendix A). Unique sample codes, consisting of the date, station name and sample depth code, will be assigned at the time of collection and recorded on the custody forms as well as on the field datasheet and on the sample container. A second unique sample number will be assigned at the laboratory and recorded on the custody forms, a copy of which will be retained by Program staff.

The analytical laboratory will provide data in agreed-upon electronic form. Electronic results files allow for direct transfer into the Program's database, eliminating the need for any manual data entry. The electronic report package will include a cover letter from the lab that notes any problems (e.g. lab accidents, QA standards or holding times exceeded, etc) or unusual results and what, if anything, was done to confirm such values (e.g. if a sample was re-analyzed, etc.). The report package from the laboratory will also include the QA/QC data and copies of chain-of-custody forms that accompanied the samples. This report package should be submitted to the Program within 60 days of the receipt of all samples from a particular cruise. The laboratory will retain raw data files, including notebooks, calibration and calculation records. The Laboratory SOP (Appendix B) contains specific requirements for holding times and number and type of QC samples for each variable.

Section B: Data Generation and Acquisition

B1 Sampling Process (Experimental) Design

The Long Island Sound Ambient Water Quality Monitoring Program (the “Program”) is an established year-round monitoring program made up of two distinct surveys. The Monthly Water Quality Monitoring Survey (the “Monthly Survey”), and the Summer Hypoxia Monitoring Survey (the “Hypoxia Survey”).

Both surveys will continue to monitor established fixed stations (Table A-1). Stations will be located with the use of a programmable GPS system. Actual latitude/longitude coordinates at the time of CTD deployment will be recorded on the field data sheet.

All measurements are considered critical to the goal of establishing a long-term dataset capable of revealing potential influences and trends of water quality in Long Island Sound.

Instantaneous water column profiles will be obtained at every station visit with the use of a Sea-Bird SeaCat Model SBE-19 or similar multi-parameter water quality monitoring instrument. These profiles will provide measurements of depth, water temperature, conductivity/ salinity, dissolved oxygen concentration, pH, light attenuation by PAR (quantum) sensor, and chlorophyll. Surface water clarity will be evaluated with a 20 cm Secchi Disk.

Monthly Survey

The Monthly Survey will involve field sampling once per month at each of 17 fixed stations (Figure A-1 and Table A-1). Twelve stations are located along the deep-water axial transect of the Sound, beginning at Station A4 in the Western Narrows to the west, and extending eastward to Station M3 in the Race. Five stations are shallower, laterally placed stations in the Western and Central Basins.

In addition to the common field data/samples noted above, discreet surface and bottom water samples will be taken for dissolved and particulate nutrients (nitrogen, phosphorus, carbon and silica), chlorophyll *a*, suspended solids, and BOD analyses (Tables A7-1 and A7-2).

Hypoxia Survey

The Hypoxia Survey will involve field sampling approximately every other week beginning in late June through early September, for a minimum of six sampling events. Three of these surveys overlap with, and will be performed in conjunction with Monthly Survey events. A seventh survey will be conducted in mid-September only if dissolved oxygen concentrations less than 3.5 mg/L are observed during the early September survey. Forty-eight fixed stations, concentrated in the Eastern Narrows and Western and Central Basins, and including the seventeen Monthly Survey sites will be sampled (Figure A6-1 and Table A6-1). These stations are concentrated in the western Sound, where low dissolved oxygen conditions have typically been most severe. An effort will be made to sample as many stations as possible given constraints of time and weather conditions. In some cases, when no hypoxia is observed in the western Sound or when the pattern of dissolved oxygen concentrations

is evident from stations sampled (*e.g.*, a large area of western or central LIS with dissolved oxygen concentrations above 5.0 mg/L), stations in the far eastern part of the Sound, where dissolved oxygen concentrations generally do not fall below 5.0 mg/L, may not be sampled.

B2 Sampling Methods

A full description of sampling methods is given in Appendix A.

Field Measurements

Field measurements are to be obtained according to the procedures outlined in *Long Island Sound Ambient Water Quality Monitoring Program, Water Quality and Hydrographic Surveys, Standard Operating Procedures Manual, 2017* (Program SOP) (Appendix A).

The field measurements to be made include the following:

1. A vertical water column profile of temperature, dissolved oxygen, conductivity, pH, chlorophyll (by fluorometer), and PAR. The vertical profile starts at the surface and is continuous to the bottom. The CTD descent rate will be maintained as close to 0.2 meter/second as possible and will be monitored in real-time via the use of an on-board computer. The instrument will be programmed to record measurements at a rate of 2 per second. While upcast data is not recommended for general use and evaluation because optimal sensor (particularly dissolved oxygen) performance is not obtained, the upcast data will provide a duplicate profile of temperature, salinity, and PAR.
2. Maximum visible Secchi disk depth.

Hydrographic Profile

Water column profiles will be obtained at each station with the use of a SeaBird Seacat model SBE-19 profiling instrument (CTD), or similar multi-parameter water quality monitoring instrument. Details on operation, calibration, and maintenance of the CTD system can be found in the Program SOP (Appendix A).

Water quality variables to be measured include temperature, conductivity/salinity, dissolved oxygen, pH, photosynthetically-active radiation (PAR), and chlorophyll *a*, all as a function of depth. The CTD will generally be mounted on a General Oceanics Rosette Multibottle Array and deployed from the stern of the 50 ft Research Vessel *John Dempsey* with the use of a hydraulic net reel. When circumstances do not allow the use of the array, the CTD will be deployed in a cage from a starboard winch. Prior to conducting the downcast, the CTD will be allowed a minimum three-minute “soak”, fully submerged near the surface. This soak time allows the internal pump to turn on and allows all sensors to stabilize and come to equilibrium with water conditions. The CTD downcast will then be conducted at a target rate of 0.2 meter/second, non-stop until the array reaches the bottom.

Water Sample Collection

Water samples will be collected with the use of 5-liter Niskin water sampling bottles. The sampling bottles will generally be mounted on the General Oceanics Rosette Multibottle Array that allows for remote actuation of the sampling bottles. Sample bottles will be filled during the upcast. When

circumstances do not allow the use of the array, sampling bottles will be mounted on a wire controlled by a starboard winch, and triggered with messengers. Details on the handling and maintenance of the sampling bottles and the array, as well as details of sample handling can be found in the Program SOP (Appendix A).

Monthly Survey

For the Monthly Survey, samples will be collected from two depths at each station for nutrient analyses. Bottom samples will be collected 3-5 meters above the sediment and surface samples will be collected two meters from the surface. Sampling bottles will be filled at each depth, consecutively, within seconds of each other, by remote actuation of sample bottles mounted on the array.

Sample processing

Grab water samples collected with the Niskin bottles will be filtered (ideally on board the research vessel in the ship's onboard laboratory) prior to delivery to the analytical lab for particulate carbon/particulate nitrogen (PC/PN), chlorophyll-a (Chl-a), total suspended solids (TSS), particulate phosphorus (PP), and biogenic silica BioSi. Filters will be stored in the onboard lab freezer until delivery to the lab at the end of the day.

Filtrate will be collected for dissolved fraction analyses of ammonium (NH₄), nitrate+nitrite (NO₃+NO₂ or NO_x), total dissolved nitrogen (TDN), dissolved inorganic phosphorus/orthophosphate (DIP or PO₄=), total dissolved phosphorus (TDP), dissolved organic carbon (DOC), and dissolved silica (SiO₂) analysis.

All containers, including filtering flasks, that will come into contact with filtrate will be sample rinsed at least three times. This filtrate will be put into sample-rinsed labeled poly bottles provided by the analytical laboratory, and chilled or frozen for preservation in the onboard freezer until sample delivery to the lab at the end of the day. Whole water samples for BOD analysis will be drawn directly from Niskin sample bottles into one-half gallon poly jugs provided by the laboratory and chilled.

Details of sample processing is contained in the Program SOP (Appendix A).

Table B2-1. Summary of field methods for Long Island Sound Ambient Water Quality Monitoring Program basic water quality variables (see Program SOP, Appendix A).

<u>VARIABLE</u>	<u>FIELD METHOD</u>	<u>APPARATUS</u>	<u>UNITS</u>
Depth	Water column profile	SeaBird SBE-19 (CTD) or YSI EXO2	Meters
Water Temperature	Water column profile	SeaBird SBE-19 (CTD) or YSI EXO2	°C
Conductivity/ Salinity	Water column profile	SeaBird SBE-19 (CTD) or YSI EXO2	PSU
PAR	Water column profile	Li-Cor Model LI-193SA Spherical Quantum Sensor as module on CTD	$\mu E/m^2/sec$
Chlorophyll <i>a</i>	Water column profile	WETLabs WETStar Fluorometer as module on CTD or YSI EXO2	mg/L
Dissolved Oxygen	Water column profile	SBE-23 sensor with modified YSI 5739 oxygen probe as module on CTD or YSI EXO2	mg/L
Surface Water Clarity	Secchi depth	20 cm Secchi disk	Meters
pH	Water column profile	YSI EXO2	pH

All procedures for handling the CTD or alternate sensor/profiling unit(s), and Niskin bottles, and all procedures for Winkler titrations and filtering are documented in the Program SOP (Appendix A). All personnel that will assist with this monitoring will be required to review the SOP prior to participating in a survey, and all personnel will be supervised, at a minimum, the first two times any new task is performed. A copy of the SOP will always be present on the research vessel should a staff member need to refer to it. Sample processing and handling protocols related to the laboratory analyses for nutrients and chlorophyll *a* are specified by the analytical laboratory and included in the relevant laboratory guidance/SOP documentation (Appendix B). Operating procedures for blanks, spikes and replicates are also included in the laboratory SOPs.

The shipboard laboratory will provide freezer and chilled storage space, and the capability to filter small volume samples. Supply of small volume bottles and all necessary filters will be the responsibility of the analytical laboratory.

B3 Sample Handling and Custody

Field Data Recording

Field crews will record most of the raw field data on hardcopy datasheets (Appendix A). The CTD profiling instruments have internal electronic file storage, and these files, if not recovered directly to the onboard computer in real-time, will be downloaded following the cast. All field data that is not in electronic form will be transcribed into an electronic database format generally within one week of the survey end date. The Program database has a Field Data Sheet Entry Form (Appendix A), to be used for all data entry that closely matches the hardcopy forms. All data entry will be performed twice. The two comparable entry logs will then be run through an in-house macro that compares each datum. Any differences between the two entries will cause a review of the hardcopy Field Data Sheet to determine the correct datum. The Field Datasheet Table in the database will then be updated with the final corrected Entry Form.

Sample Identity Codes

All station visits will be uniquely identified by the Station Name and the Cruise Name. In the Program database these two items are consistently used as primary keys; they are required and no matching combinations are allowed. All nutrient data will be further identified by the Depth Code (“S” for Surface, “B” for Bottom) and the Variable measured. Samples containers to be used to store and deliver samples to the nutrient analytical lab will be pre-labeled with Station Name, Depth Code, Cruise Name, and, where necessary, the variable/variables to be measured. Packages used to store and transport PC/PN and Chlorophyll-*a* filters, for example, are identical, so that these labels must specify the variable. The date the sample is taken will be added to the containers in the field.

Chain of Custody Forms

Sample chain-of-custody (COC) forms will accompany each delivery of samples to the analytical laboratory. COC forms will generally be prepared ahead of time with Station Names and Depth Codes (e.g. B3S = Station B3 Surface water) based on the typical three or four-day station visit plan. The volume of sample filtered, where applicable, and the filter identification number for TSS samples will be recorded on the COC forms by the field crew. The laboratory will log in all samples when they take possession, assigning a unique laboratory ID number to each unique sample. Laboratory ID numbers will be recorded by the laboratory staff directly on the COC forms and a completed copy returned to Program staff.

Table B3-1. General summary of sample containers, preservation, and holding times for the Long Island Sound Ambient Water Quality Monitoring Program water quality indicators sample analyses (see Program SOP, Appendix A, and Laboratory SOPs, Appendix B, attached). Sample container volume may vary as per laboratory.

<u>VARIABLE</u>	<u>SAMPLE TYPE</u>	<u>SAMPLE CONTAINER</u>	<u>PRESERVATION METHOD</u>	<u>HOLDING TIME</u>
Ammonia (NH₃)	Filtrate	250-ml poly bottle with lid (single filtrate bottle used for six variables; or as per lab)	Sample frozen	14 days
Nitrate + Nitrite (NO₃⁻) + (NO₂⁻)	Filtrate	250-ml poly bottle with lid	Sample frozen	28 days
Total Dissolved Nitrogen (TDN)	Filtrate	250-ml poly bottle with lid	Sample frozen	28 days
Particulate Nitrogen (PN)	25mm 0.7um GF/F filter	aluminum foil packet; 2 duplicate filters per packet	Sample frozen	28 days
Orthophosphate (PO₄³⁻)/ Dissolved Inorganic Phosphorus (DIP)	Filtrate	250-ml poly bottle with lid	Sample frozen	48 hours
Total Dissolved Phosphorus (TDP)	Filtrate	250-ml poly bottle with lid	Sample frozen	28 days
Particulate Phosphorus (PP)	47mm 0.7um GF/F filter	aluminum foil packet; 2 duplicate filters per packet	Sample frozen	28 days
Dissolved Organic Carbon (DOC)	Filtrate	250-ml poly bottle with lid	Sample frozen	28 days
Particulate Carbon (PC)	25mm 0.7um GF/F filter	aluminum foil packet; 2 duplicate filters per packet	Sample frozen	28 days
Dissolved Silica (SiO₂)	Filtrate	125-ml poly bottle with lid	Sample chilled/frozen	28 days
Particulate (Biogenic) Silica (BioSi)	47mm 0.4um polycarbonate filter	50-ml poly centrifuge tube with lid	Sample frozen	28 days
Chlorophyll <i>a</i> (Chl a)	25mm 0.7um GF/F filter	aluminum foil packet; 2 duplicate filters per packet	Sample frozen	30 days
Total Suspended Solids (TSS)	47mm 0.7um GF/F filter	pre-labeled, filter-specific aluminum cup	Sample frozen	7 days
Biological Oxygen Demand (BOD)	Whole water	1.89 liter poly jug with lid	Sample chilled	24 hours

B4 Analytical Methods

Filters, filtrate, and whole water samples prepared on the research vessel (see Program SOP, Appendix A) will be delivered daily, or frozen and shipped immediately following a the completion of a 3-4 day survey, to the nutrient analytical laboratory. The Laboratory will conduct all analyses in accordance with generally accepted laboratory procedures and in keeping with their SOP (Appendix B). Appropriate QC samples will be run with each batch of samples, typically all the samples from a single cruise. Table B4-1 summarizes field and analytical methods and associated detection limits.

Table B4-1. Summary of field and analytical methods for Long Island Sound Ambient Water Quality Monitoring Program water quality indicators sample analyses (see Program SOP, Appendix A, and Laboratory SOP, Appendix B).

<u>VARIABLE</u>	<u>FIELD METHOD</u>	<u>ANALYTICAL METHOD</u> description and Method Ref. No.	<u>DETECTION</u> <u>LIMIT</u>
Ammonia (NH₃)	Filtration, generally 500mL; 47mm/0.7um GF/F; filtrate frozen	automated ion analyzer/colorimetric; EPA 350.1	0.002 mg/L
Nitrate + Nitrite (NO₃⁻) + (NO₂⁻)	Filtration, generally 500mL; 47mm/0.7um GF/F; filtrate frozen	automated ion analyzer/colorimetric; EPA 353.2	0.002 mg/L
Total Dissolved Nitrogen (TDN)	Filtration, generally 500mL; 47mm/0.7um GF/F; filtrate frozen	persulfate oxidation; automated ion analyzer/colorimetric; EPA 353.2	0.040 mg/L
Particulate Nitrogen (PN)	Filtration, generally 200mL; 25mm/0.7um GF/F; filter frozen	high temperature combustion; CHN elemental analyzer; EPA 440.0	0.010 mg/L
Orthophosphate (PO₄³⁻)/ Dissolved Inorganic Phosphorus (DIP)	Filtration, generally 500mL; 47mm/0.7um GF/F; filtrate frozen	automated ion analyzer/colorimetric; EPA 365.2	0.002 mg/L
Total Dissolved Phosphorus (TDP)	Filtration, generally 500mL; 47mm/0.7um GF/F; filtrate frozen	persulfate oxidation; automated ion analyzer/colorimetric; EPA 365.1	0.002 mg/L
Particulate Phosphorus (PP)	Filtration, generally 200mL; 25mm/0.7um GF/F; filter frozen	acid (HCl) extraction; automated ion analyzer/colorimetric; EPA 365.1	0.001 mg/L
Dissolved Organic Carbon (DOC)	Filtration, generally 500mL; 47mm/0.7um GF/F; filtrate frozen	high temperature combustion; non- dispersive infrared analyzer; EPA 415.1	0.5 mg/L
Particulate Carbon (PC)	Filtration, generally 200mL; 25mm/0.7um GF/F; filter frozen	high temperature combustion; CHN elemental analyzer; EPA 440.0	0.010 mg/L
Dissolved Silica (SiO₂)	Filtration, generally 200mL; 47mm/0.4um polycarbonate filter; filtrate chilled	automated ion analyzer/colorimetric; EPA 370.1	0.025 mg/L
Particulate (Biogenic) Silica (BioSi)	Filtration, generally 200mL; 47mm/0.4um polycarbonate filter; filter frozen	heated NaOH digestion; automated ion analyzer/colorimetric; EPA 370.1	0.010 mg/L
Chlorophyll <i>a</i> (Chl a)	Filtration, generally 200mL; 25mm/0.7um GF/F; filter frozen	CH ₃ COCH ₃ (MgCO ₃) extraction; fluorometric analysis; EPA 445.0	0.075 ug/L
Total Suspended Solids (TSS)	Filtration, generally 500mL; 47mm/0.7um GF/F; filter frozen	gravimetric; EPA 160.2	1.0 mg/L
Biological Oxygen Demand (BOD)	whole water sample chilled	oxygen consumption via dissolved oxygen measurements at intervals from 5 through 30 days	0.5 mg/L

B5 Quality Control

Field QC Requirements

Field QC is associated with site location, collection and handling of water samples, and direct measurements including the CTD profile and Secchi depth.

Station Location

Navigation throughout the survey period will make use of vessel-mounted differential GPS. Sampling location will be recorded while the CTD unit is coming to equilibrium, or “soaking”, in the surface water, just prior to the start of the downcast, as coordinates of latitude/longitude in degrees-minutes, expressed to the nearest 0.01 minute (i.e., 00°00.00'). Horizontal accuracies of 0.02 nautical miles are expected with repeatability in excess of this value.

In cases where equipment deployment may pose some risk to Program vessel or equipment, or to another's property, the crew is allowed to relocate to the nearest location of similar depth ($\pm 20\%$) where sampling can be conducted without unusual risk. This can occur, for example, when lobster pot strings are deployed near a station.

CTD Water Column Measurements (Sea-Bird SBE-19)

The quality control related to CTD use includes routine calibration and maintenance. Basic parameters of pressure/depth, temperature, and conductivity/salinity are calibrated annually by the manufacturer (Sea-Bird, Inc.). The calibration report includes the degree of drift since the last calibration, and their reliability has been excellent within the one to two decimal places of interest to the Program. A QC check of depth is provided daily by the research vessel depth finder. Component PAR sensor is also calibrated by the manufacturer (Li-Cor, Inc.), on their recommended schedule of once every two years.

In August 2010, CT DEEP upgraded the dissolved oxygen sensors on its CTDs to the Sea-Bird SBE 43 Dissolved Oxygen Sensor, a polarographic membrane sensor. The sensor is returned to the manufacturer annually for calibration. Following the manufacturer's guidelines, pre-survey checks of the sensor are performed and compared to values obtained through Winkler titrations. If the sensor has drifted more than 0.2 mg/L the calibration coefficients can be adjusted to the Winkler results. If the adjustment is greater than 20% the unit should be returned to Sea-Bird for recalibration

In August 2010, CT DEP also upgraded its CTDs to include pH sensors. The SBE 18 pH sensor is an add-on auxiliary sensor for profiling CTDs. The sensor uses a pressure-balanced glass electrode/Ag/Ag-Cl reference pH probe to provide *in situ* measurements at depths up to 1200 meters. The pH sensor is returned to the manufacturer for annual calibration along with the CTD. Additionally, the pH sensor is calibrated using a 3 point calibration prior to every survey and the calibration coefficients can be adjusted as necessary.

CTD Water Column Measurements (YSI EXO2)

In 2017, new YSI EXO2 units are being used concurrently with the SBE-19, with the ultimate goal of switching to the YSI units. This change has been undertaken due to age of the SBE-19s, and the difficulty of updating, as well as the prevalence of the YSI instrumentation in other monitoring programs. The YSI units have the added advantage of sensors that are field-replaceable, helping to minimize data gaps due to sensor failures.

Data is being collected concurrently to compare performance and data comparability between the two units, before employing the YSI units as the primary CTD.

The YSI EXO2 units will be calibrated annually (temperature, salinity), with other parameters (dissolved oxygen) calibrated prior to and/or after each survey. SOPs specific to the use of the YSI EXO2 are currently in development.

Table B5-1. Measurement quality objectives and quality assurance sample information for field water column observations.

Variable	QA Sample Type	Frequency of QA	Data Generated
Field Measurements			
Depth	Performance verification at certified calibration facility	Annually	CTD response vs. calibration standards; annual drift
Depth	QC check against vessel's depth finder	Every cast	Difference between CTD station depth and on-board depth finder
Temperature	Performance verification at certified calibration facility	Annually	CTD response vs. calibration standards; annual drift
Salinity	Performance verification at certified calibration facility	Annually	CTD response vs. calibration standards; annual drift
Dissolved Oxygen	New membrane installation and calibration	At least monthly; always prior to cruise	100% saturated water; new coefficient values
Dissolved Oxygen	Winkler replicates as part of sensor calibration	At least monthly; always prior to cruise	precision
pH	3-point QC check with standard buffers (4.0, 7.0, 10.0)	At least monthly; always prior to cruise	Difference between probe and standard

Table B5-2. Measurement quality objectives and quality assurance sample information for laboratory analyses.

Variable	QA Sample Type	Frequency of QA
Analytical Laboratory Measurements		
Ammonia (NH₃)	Standards, spikes, lab and field duplicates	10% per batch/cruise
Nitrate + Nitrite (NO₃⁻+NO₂)	Standards, spikes, lab and field duplicates; QC check against Day 0 whole water BOD sample at up to 10 stations	10% per batch/cruise
Total Dissolved Nitrogen (TDN)	Standards, spikes, lab and field duplicates	10% per batch/cruise
Particulate Nitrogen (PN)	Field blanks and field duplicates	10% per batch/cruise
Orthophosphate (PO₄³⁻) or (DIP)	Standards, spikes, lab and field duplicates	10% per batch/cruise
Total Dissolved Phosphorus (TDP)	Standards, spikes, lab and field duplicates	10% per batch/cruise
Particulate Phosphorus (PP)	Standards, spikes, field blanks, lab and field duplicates	10% per batch/cruise
Dissolved Org. Carbon (DOC)	Standards, spikes, lab and field duplicates	10% per batch/cruise
Particulate Carbon (PC)	Field blanks and field duplicates	10% per batch/cruise
Dissolved Silica (SiO₂)	Standards, spikes, lab and field duplicates	10% per batch/cruise
Biogenic Silica (BioSi)	Standards, spikes, field blanks, lab and field duplicates	10% per batch/cruise
Chlorophyll <i>a</i> (Chl a)	Standards, spikes, field blanks, field duplicates	10% per batch/cruise
Total Suspended Solids (TSS)	Standards, field blanks and duplicates; replicates averaged	10% per batch/cruise
Biological Oxygen Demand (BOD)	Field duplicate	10% per batch/cruise

B6 Equipment Testing, Inspection and Maintenance

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.

B7 Instrument/Equipment Calibration and Frequency

Calibration Procedures

Field Equipment

SeaBird CTD Profiler Units

The shipboard instruments will be maintained in accordance with the guidelines provided by the manufacturer. The Sea-Bird CTD profiles will be serviced annually at a certified facility. The profilers will be returned to the manufacturer at approximately 1-year intervals for conductivity, temperature and depth calibration, and general maintenance as recommended by the manufacturer. Two identical CTD units are available and are identified by unique numbers so that maintenance or factory calibration will not affect the survey schedule as they will be on alternate maintenance schedules.

The dissolved oxygen sensor will be calibrated at least monthly, prior to each monthly survey, according to the manufacturer's instructions. For each field instrument a maintenance notebook is maintained, including all calibration records.

Other similarly equipped profiling units and/or individual units or sensors will be operated, maintained, and serviced in accordance with the guidelines provided by the manufacturer.

Laboratory Equipment

All laboratory instrument usage, maintenance, calibration, troubleshooting and service are performed according to the procedures documented in each laboratory's SOP (current versions attached as Appendix B). All chemicals are obtained from the instrument manufacturer or from vendors of scientific supplies. Where appropriate, an instrument logbook is used to record all maintenance and calibration activities.

B8 Inspection of Supplies

Field supplies with definite shelf life will have expiration dates recorded directly on the container and stock will be rotated to ensure the availability of fresh chemicals at all times. An inventory of chemicals and supplies on the research vessel (see Appendix A) allows field staff to ensure that a record of supplies needed is available for subsequent survey preparation activities.

Laboratory supplies and stock solution preparations are documented in each laboratory's SOP (Appendix B).

B9 Nondirect Measurements

The only nondirect measurement data to be used will be those data previously collected by the Program. These data collected using the same methods and under previously approved QAPPs,

are used during data review and assessment as they provide for expected parameter ranges. Such provision is not absolute however; previously observed ranges are used only as a guide. No datum will be rejected solely because it does not fall within the previously measured range.

B10 Data Management

All Program data will be managed in an established, electronic Program database.

Field Data

Field crews will record most of the raw field data on hardcopy datasheets (Appendix B). The CTD profiling instruments have internal electronic file storage, and these files, if not recovered directly to the onboard computer in real-time, will be downloaded following the cast. Data from manual Winkler dissolved oxygen titrations will be recorded on the Field Data Sheet by the field technician. All field data that is not in electronic form will be transcribed into an electronic database format generally within one week of the survey end date. The Program database (in Microsoft Access) has a Field Data Sheet Entry Form (Appendix B), to be used for all data entry that closely matches the hardcopy forms. All data entry will be performed twice. The two comparable entry logs will then be run through an in-house macro that compares each datum. The process is tracked by forms designed to ensure that all data are reviewed completely (Appendix B). Any differences between the two entries will cause a review of the hardcopy Field Data Sheet to determine the correct datum. Once data are verified to have been entered correctly, they are uploaded to the database and the Field Datasheet Table in the database is updated with the final corrected Entry Form.

Sample Identity Codes

All station visits will be uniquely identified by the Station Name and the Cruise Name. In the Program database these two items are consistently used as primary keys; they are required and no matching combinations are allowed. All nutrient data will be further identified by the Depth Code (“S” for Surface, “B” for Bottom) and the Variable measured. Samples containers to be used to store and deliver samples to the analytical laboratory will be pre-labeled with Station Name, Depth Code, Cruise Name, and, where necessary, the variable/variables to be measured. Packages used to store and transport PC/PN and Chlorophyll-*a* filters, for example, are identical, so that these labels must specify the variable. The date the sample is taken will be added to the containers in the field.

Chain of Custody Forms

Sample chain-of-custody (COC) forms will accompany each delivery of samples to the analytical laboratory (Appendix B). COC forms will generally be prepared ahead of time with Station Names and Depth Codes (e.g. B3S = Station B3 Surface water) based on the typical three or four-day station visit plan. The volume of sample filtered, where applicable, and the filter identification number for TSS/PP samples will be recorded on the COC forms by the field crew.

The laboratory will log in all samples when they take possession, assigning a unique laboratory ID number to each unique sample. Laboratory ID numbers will be recorded by the laboratory

staff directly on the COC forms and a completed copy returned to Program staff.

Data Transformation

Field CTD dissolved oxygen data are transformed with the use of manufacturer-provided software. The complete process is described in the *Guide to CTD Data Processing*, Appendix A. The transformation process is automated so that little if any judgment of the data handler is required. In any case, only very qualified technical staff with significant experience with these files are allowed to conduct this data transformation task. Unusual or errant data require the ability gained from extensive experience and understanding of the data files. Transformed data are reported in the database as *Corrected Oxygen*, along with the original, raw oxygen data, so that data users may employ their own transformation if they desire.

Laboratory Data Validation

Procedures for laboratory data validation are contained in the each laboratory's SOP (current laboratory SOP, UCONN/CESE, Appendix B). After having undergone all validation procedures at the laboratory, the data are provided to the CTDEEP Program staff.

Analytical and related quality control data are entered and validated by the Program data management personnel. Generally, the electronic files received from the analytical laboratory are compatible with the Program database.

Section C: Assessment/Oversight

C1 Assessments and Response Actions

Field operations lead will be responsible for field and data-entry staff training, review of field and data processing performance, and making corrections. The quality assurance officer will perform regular data review and report issues to the field/database lead. The technical project supervisor will be responsible for field and office audits to ensure that data collections and manipulation are ongoing and in adherence to the quality assurance plan.

C2 Reports to Management

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. Summertime Hypoxia Survey progress will be reported via biweekly cruise summaries.

Section D: Data Validation and Usability

D1 Data Review, Validation, and Verification

Section B10, Data Management, describes all data handling procedures in the field, laboratory, and program office that lead to survey data ultimately becoming part of the Program database.

Once data are uploaded to the electronic database, Program staff review the data for completeness, outlying or suspect values, comparability of nutrient parameters (TDN > NH₃ + NO_x, etc.), and to apply any problem codes necessary to the data. Problem data are flagged, but reported values generally remain in the database. Each flag includes a description of the apparent or suspected problem with the datum. All problem data are reported to laboratory QA staff with a request for a) repeat of sample analysis if an archived sample is available; or b) a review of associated laboratory documentation to confirm the reported result.

After being scrutinized during the data entry phase, data are analyzed and plotted to examine any outliers or anomalies. These are examined, verified and corrected if necessary. Field audits are performed by the Field operations lead to assure that all data are collected according to standard operating procedures, and that the collection effort is consistent. All field logs and information will be thoroughly reviewed prior to data analysis to assure that all data were collected uniformly. Any datum collected outside of the standard operating procedures will be examined to determine whether it is representative.

All quality assurance data and reports will be examined prior to data analysis to verify that data were properly and consistently collected. Any deviations in data collection will be taken into account during data analysis. All calibration logs will be examined to determine how well the measurement instruments performed. If there appears to be significant drift in instrument performance, it will be determined whether an adjustment is possible. All raw data files will be kept in paper files. Original (unmanipulated) data will be retained by CTDEEP.

With the exception of the CTD data transformation described in Section B10, above, data reduction will only occur as part of a data report where data are summarized for ease of presentation and to focus on patterns and trends. The Program database, in its entirety, will continue to be available upon request. It is also a goal of the Program to upload all validated data to EPA's STORage and RETrieval (STORET) data warehouse within 1 year of collection for wider public dissemination of the data collected by the program.

D2 Validation and Verification Methods

All required field data will be entered directly onto field data sheets. All data sheets will be validated in the field for accuracy. The data sheets from a single cruise will be maintained in Program files together with a *Data Processing Cover Sheet* (Appendix A) that documents the status of CTD data processing to the Program database.

The consistent application of methods provided in the Program SOPs (Appendix A) and this QAPP provides good certainty that the data are both valid and usable. Any missing samples or laboratory accidents 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.

Any unusual observations will be reviewed by CTDEEP staff involved in the project and, if warranted, outside expertise will be consulted to resolve any problems with data validation and usability.

D3 Reconciliation with Data Quality Objectives

Each survey's data will be reviewed by DEEP Program staff for completeness, compliance with QAPP, correctness, and consistency. Unusual or unexpected results will be reviewed and a determination made as to data usability. Data summaries including annual means, seasonal and long term trends will be reviewed and evaluated for long term project success. Data will be made available upon request to EPA or designees for further review.

APPENDIX A

CTDEEP Long Island Sound Ambient Water Quality Monitoring Program Standard Operating Procedures Manuals

(including Field procedures, Field datasheets, Chain-of-Custody Forms/delivery records,
Field data processing procedures, CTD Data processing guide, Database forms, etc.)

APPENDIX B
Contract Laboratories
Laboratory SOP

INSERT

University of Connecticut
Center for Environmental Science and Engineering
Laboratory Standard Operating Procedures