

**Quality Assurance Project Plan  
for  
Plymouth Ponds and Lake Stewardship Program**

**Prepared by  
Town of Plymouth  
Department of Marine and Environmental Affairs  
Kim Tower - Environmental Technician  
26 Court Street, Plymouth MA 02360**

*This Quality Assurance Project Plan was generated by AquaQAPP, a tool managed by Massachusetts Bays National Estuary Partnership and developed with funding from the United States Environmental Protection Agency and the Massachusetts Department of Environmental Protection.*

Date generated: September 19th, 2023

**Disclaimer:** This plan was generated by AquaQAPP, a web-based application created by the Massachusetts Bays National Estuary Partnership (MassBays). AquaQAPP generates tailored Quality Assurance Project Plans (QAPPs) for marine and freshwater water quality and benthic monitoring efforts in the Commonwealth of Massachusetts and is intended to assist volunteer monitoring programs in collecting quality-assured data.

This plan does not define, or otherwise limit, the purpose for which organizations may seek to use the plan or apply their data. A goal of the AquaQAPP project, however, is to bring more citizen science data to decision makers, including MassBays, the Massachusetts Department of Environmental Protection (DEP), and the Environmental Protection Agency (EPA).

Use of AquaQAPP is not required. Using AquaQAPP to document and plan for collection of quality assured data, produces a QAPP that is considered pre-approved by DEP and which should be acceptable to EPA, therefore agency review is not required prior to sampling. This pre-approval is valid so long as samples are collected and analyzed in strict accordance with the QAPP generated by the application which itself has not been significantly altered from the original output. "Not significantly altered" means that the user has not made or will not make changes to sample collection protocols, analytical methods, or other substantive content included in the generated QAPP. Changes such as addition of project roles and responsibilities, or additional detail regarding data quality indicators are not considered significant alterations.

Where new or revised methods, additional parameters, or other substantial changes are included beyond the content generated by AquaQAPP, and a stated objective of the monitoring effort is to submit the resulting data to DEP, DEP requires QAPP review prior to implementation. The modified QAPP can be submitted to:

Suzanne Flint (Suzanne.Flint@mass.gov)  
Bureau of Water Resources, Watershed Planning Program  
Massachusetts Department of Environmental Protection  
8 New Bond Street, Worcester, MA 01606

DEP retains sole discretion as to what extent the agency will use data or information produced or resulting from use of this document.

Note that for any projects funded by their agencies, both DEP and EPA still require QAPP review prior to sampling. Monitoring programs funded by EPA or DEP must follow agency requirements for quality assurance, and a QAPP generated with AquaQAPP may or may not meet those requirements. QAPPs for monitoring programs to support or influence discharge permits or TMDLs will also require additional review. Please check with the funding agency for guidance in these cases.

## Section A. Project Management Elements

### A1 Title and Certification Page

Plan Title: Plymouth Ponds and Lake Stewardship Program

Name of Individual: Town of Plymouth  
Preparing QAPP and Name of Organization(s): Department of Marine and Environmental Affairs  
Kim Tower - Environmental Technician  
Implementing Project: 26 Court Street, Plymouth MA 02360

Effective Dates of Plan: 2023-2026

#### Research Assistant:

Name: Sara J. Horvet Phone: 508-910-6325  
Signature: 

Date: 10/11/23

#### Sr. Research Associate:

Name: David White PhD Phone: 508-910-6325  
Signature: 

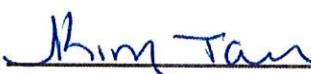
Date: 10/11/2023

#### Primary Contact:

Name: Kim Tower Phone: 508-747-1620  
Signature: 

Date: 10-4-23

I Kim Tower certify that Town of Plymouth  has  not made changes to methods, or added monitoring parameters beyond the content generated by AquaQAPP and further certify that I have read and understood the auto-generated content contained herein

Signature: 

Date: 10-4-23

## A2 Table of Contents

<b>Section A. Project Management Elements.....</b>	<b>3</b>
A1    Title and Certification Page .....	3
A2    Table of Contents .....	4
A3    Distribution List .....	7
A4    Program Organization and Task Responsibilities .....	8
A5    Problem Definition/Background .....	9
A5.1    Problem Definition.....	9
A5.2    Problem Background .....	9
A6    Project Description and Timeline .....	9
A6.1    Project Description .....	9
A6.2    Map(s) of Area, Waterbody, and Sampling Sites.....	10
A6.3    Anticipated Schedule.....	11
A7    Data Quality Objectives.....	11
A8    Training Requirements .....	13
A9    Documentation and Records.....	13
A9.1    Documentation .....	13
A9.2    Field Records.....	14
<b>Section B. Fresh Water/Water Quality Data Generation and Acquisition.....</b>	<b>16</b>
B1    Sampling Design .....	16
B1.1    Sampling Site Selection.....	16
B1.1    Sample Site Selection.....	16
B1.2    Location .....	16
B1.3    Sample Collection Methods.....	16
B2    Sampling Methods: Sample Collection and Storage .....	21
B2.1    Water Quality Monitoring .....	22
B3    Sample Handling and Custody.....	22
B4    Analytical Methods.....	23
B5    Field and Analytical Laboratory Quality Control .....	24
B5.1    Field Duplicates and Field Blanks.....	24
B6    Instrument/Equipment Inspection and Testing .....	26
B7    Field Equipment/Maintenance, Inspection, and Calibration .....	27
B7.1    Pre-measurement Instrument Checks and Calibration .....	27

B7.2	Post-measurement Calibration Check—Multi-Parameter unit .....	28
B7.3	Instrument/Equipment Inspection, Testing Procedures .....	28
B8	Inspection/Acceptance of Supplies and Consumables.....	28
B9	Data Acquisition Requirements.....	29
B10	Data Management.....	29
B10.1	Process and Procedures.....	29
B10.2	Data Handling .....	29
B10.3	Management Requirements.....	30
<b>Section C. Assessment and Oversight .....</b>	<b>30</b>	
C1	Assessment and Response Actions .....	30
C1.1	Assessments.....	30
C1.2	Assessment Findings and Corrective Action Responses .....	31
C2	Reports .....	32
<b>Section D. Data Review and Usability.....</b>	<b>33</b>	
D1	Data Review and Validation .....	33
D2	Verification and Validation Methods .....	33
D3	Reconciliation with User Requirements .....	34
D3.1	Comparison to Measurement Criteria.....	35
D3.2	Overall Assessment of Environmental Data .....	36

## **List of Attachments**

ATTACHMENT A: Map(s) of Sampling Locations

ATTACHMENT B: Sample Collection and Storage SOPs

ATTACHMENT C: Forms

ATTACHMENT D: Laboratory QAPP and SOPs

## **List of Tables**

Table A3.1. QAPP Distribution List.....	7
Table A4.1. Project Organization and Responsibilities .....	8
Table A6.1. Sampling Locations .....	10
Table A6.2. Program Schedule.....	11
Table A7.2. Data Quality Indicators and Acceptance Criteria (Performance Goals).....	12
Table A9.1. Record Handling Procedures .....	13
Table A9.2. Project-Specific Datasheets and Forms for All QAPPs .....	14
Table B1.1. Freshwater Quality Field Sampling Summary .....	16
Table B2.1. Equipment Preparation, Sample Processing, and Storage Requirements.....	21
Table B4.1. Approved Analytical Methods.....	23
Table B5.1. Quality Control Measures .....	25
Table B5.2. Field Quality Control (measured using sensors) .....	26
Table B5.5. Data Validation Quality Control for Water Chemistry .....	26
Table B6.1. Typical Instrument/Equipment Inspection and Testing Procedures .....	27
Table B7.1. Instrument Calibration Procedures.....	28

### A3 Distribution List

The following individuals and their respective organizations will hold copies of the approved QAPP:

**Table A3.1. QAPP Distribution List**

Project Role	Name, Organization
Project Manager, Field Coordinator	Kim Tower, Town of Plymouth
Laboratory Manager	Sara J. Horvet, UMASS Dartmouth School of Marine Science and Technology

**Name:** Kim Tower

**Title:** Environmental Technician

**Organization** Town of Plymouth

**Address:** 26 Court Street

**City:** Plymouth

**State:** MA **Zip:** 02360

**Telephone:** 508-747-1620 **Email:** ktower@plymouth-ma.gov

**Name:** Sara J. Horvet

**Title:** Research Assistant

**Organization** UMASS Dartmouth School of Marine Science and Technology

**Address:** 706 S Rodney French Blvd,

**City:** New Bedford

**State:** MA **Zip:** 02744

**Telephone:** 508-910-6325 **Email:** ssampieri@umassd.edu

## A4 Program Organization and Task Responsibilities

**Table A4.1. Project Organization and Responsibilities**

Personnel name and title	Project Role	Responsibilities
Kim Tower Environmental Technician	1. Project Manager 2. Field Coordinator	1. Overall management of administrative and technical work of the monitoring program. 2. Planning and coordination of all field monitoring. Includes technical oversight, preparation of field equipment, volunteer assignments and scheduling. Receives samples and delivers to the lab. Oversees proper sample handling/preservation and chain of custody forms.
Sara J. Horvet Research Assistant	3. Laboratory Manager	3. Provide laboratory QAPP and SOPs for attachment to the QAPP, communicate with the QA Manager regarding laboratory corrective actions, deliver corrective action files and data reports to the Project Manager.
David White PhD Sr. Research Associate	4. Data Manager 5. QA Manager	4. Data collection, management, analysis and interpretation. 5. Review of procedures and data generated including reports to ensure adherence to QAPP. Reports any problems to the Project Manager, and works with Project Manager to document and correct any deviations.

## A5 Problem Definition/Background

### A5.1 Problem Definition

The Plymouth Ponds and Lakes Program was established to form a consistent monitoring program to evaluate the general water quality health as it pertains to nutrients. The Town can then utilize the data to evaluate potential management options at each site or whether further evaluation is necessary. The data is also utilized by MassDEP to evaluate its standing in the 303d list of waterbodies. Over the last few decades citizens have become concerned of the degradation of the water quality in their ponds. In the last several years more ponds have become susceptible to cyanobacteria blooms which affect recreational uses and public health.

### A5.2 Problem Background

The Study area includes multiple ponds within Plymouth as described in the monitoring locations section. Due to limited funding and volunteers a handful of ponds will be selected each season for monitoring. The majority of the ponds are inland with phosphorus as the main water quality concern. In several ponds, cyanobacteria blooms and advisories have occurred over the last decade.

## A6 Project Description and Timeline

### A6.1 Project Description

#### *Project Objectives*

The Plymouth Pond and Lakes Stewards (PALS) program goals are to establish a consistent basis/strategy to collect water quality data from the town's ponds and provide feedback to citizens and town decision makers about pond status and management concerns. The program will be used for management purposes and is not intended for regulatory decisions. The Plymouth PALS snapshot is a monitoring program that is designed to provide initial and long term data about the status of selected ponds.

#### *Study Area*

The project area includes waterbodies within the Town of Plymouth. Each waterbody will have one designated sampling spot at the deepest spot in the pond unless otherwise noted. For ponds approximately 1m deep two surface samples will be collected. For ponds less than 9 meters deep a surface sample and 1 sample at 1m from the bottom will be collected. For ponds greater than 9 meters deep surface, 3m, 9m and 1m from bottom will be collected. In addition to the collection of water quality samples, profiles of dissolved oxygen and temperature will be collected,

#### *Time Period*

The PALS program is a long term program. The majority of sampling occurs during August/September in order to gauge what are likely to be worst water quality conditions in the ponds regularly included and other ponds selected annually based on citizen input and town priorities. This strategy is the same approach that has been used for the Cape Cod PALS snapshots for the past 20 years. For specific ponds that have had management plans, those ponds generally have increased sampling frequency occurring between April and October.

### **Parameters**

The parameters are related to water quality concerns through the collection of nutrients and chlorophyll analysis.

All parameters are measured by the School of Marine Science and Technology - CSP/SMAST Laboratory.

### **Data Users**

The program will be used for management purposes and is not intended for regulatory decisions. The Plymouth PALS snapshot is a monitoring program that is designed to provide initial and long term data about the status of selected ponds to watershed associations, residents and for DEP integrated list of waterbodies assessment. The Town will utilize the data to guide management options and future sampling plans for ponds.

### **Rationale**

Sampling locations and number of samples were determined in the initiation of the Plymouth Ponds and Lakes Stewardship Program. This program mimics the efforts and procedures of the Cape Cod Atlas Monitoring Program. In general, one location at the deepest spot in each pond is selected. For ponds less than 3M, two surface grab samples are collected. For ponds less than 9M, surface and 1M from bottom samples are collected along with profiles of temperature and dissolved oxygen. For greater than 9M, surface grab, 3M, 9M and 1M from bottom is collected. For Great Herring Pond - the management study recommended additional grab samples at 8M and 10M.

## **A6.2 Map(s) of Area, Waterbody, and Sampling Sites**

A map with sampling locations labeled is included as an attachment.

**Table A6.1. Sampling Locations**

Location ID	Location Name	Latitude/Longitude
Billington Sea West	Billington Sea West	41.934823 / -70.693134
Billington Sea East	Billington Sea East	41.932361 / -70.683583
Bloody Pond	Bloody Pond	41.847129 / -70.582671
Clear Pond	Clear Pond	41.933495 / -70.730054
Gallows Pond	Gallows Pond	41.862983 / -70.614226
Great Herring Pond	Great Herring Pond	41.803706 / -70.563197
Halfway Pond	Halfway Pond	41.852377 / -70.614276
Little Herring Pond	Little Herring Pond	41.823985 / -70.574792
Little Long Pond	Little Long Pond	41.868550 / -70.612037
Long Pond	Long Pond	41.858590 / -70.604632
Round Pond	Round Pond	41.852755 / -70.604445
Savery Pond	Savery Pond	41.847384 / -70.549685

### A6.3 Anticipated Schedule

**Table A6.2. Program Schedule**

Activity	J	F	M	A	M	J	J	A	S	O	N	D
Training				X								
Data Review	X	X	X									
Sampling				X	X	X	X	X	X	X		
Targeted Eutrophication Sampling								X	X			

### A7 Data Quality Objectives

Overall water quality health in regards to nutrients, dissolved oxygen and clarity for the ponds being monitored.

Requirements for ensuring that the data are useable for their intended purpose (that is, are of suitable quality) include accuracy, precision, representativeness, comparability, and completeness. When these requirements are met, the final data product is technically defensible. Data elements for this project are discussed in terms of the appropriate Data Quality Indicators, defined as:

<b>Accuracy:</b>	The extent of agreement between a measured value and the true value of interest.
<b>Precision:</b>	The extent of mutual agreement among independent, similar, or related measurements.
<b>Representativeness:</b>	The extent to which measurements represent true systems.
<b>Comparability:</b>	The extent to which data from one study can be compared directly to similar studies.
<b>Completeness:</b>	The measure of the amount of data acquired versus the amount of data required to fulfill the statistical criteria for the intended use of the data.

Quality indicators and criteria for acceptance for this project are listed in Table A7.2 and described below. Details of how these criteria are met for each component of the program's monitoring tasks are presented in Section B5.

#### Precision

Precision will be assessed through a measure of the degree of agreement (relative percent difference, or RPD) among replicate (e.g., duplicate) samples or repeated probe readings.

#### Accuracy

Laboratory accuracy will be established by following the policy and procedures provided in the laboratory's QAPP. Analytical accuracy objectives (i.e., for samples) include non-detectable

concentration in ambient field blanks.

#### Representativeness

Sampling locations and survey times were selected to ensure that the samples taken represent typical field conditions at the time and location of sampling.

#### Comparability

Standardized sampling and analytical methods, units of reporting, and site selection procedures will be used to ensure comparability of data with others using those same methods. Sample time and date of collection, sample storage and transfer, as well as laboratories will be documented so that future surveys can produce comparable data by following similar procedures.

#### Completeness

This project will be considered fully successful if at least 80% of the anticipated number of samples are collected, analyzed, and determined to meet data quality objectives.

**Table A7.3. Data Quality Indicators and Acceptance Criteria (Performance Goals)**

*Note: Parameters may be listed more than once; this is to indicate differing locations and/or sampling frequencies for that parameter.*

Parameter - Method	Units	Accuracy	Overall Precision (RPD)	Approx. Expected Range
Temperature - multi-parameter probe meter	Celsius (C) degrees	± 1 °C (check against NIST-certified thermometer)	± 1.0	0-35
Dissolved oxygen - multi-parameter probe meter	mg/L	± 0.2 (post-field check against 100% saturation)	± 0.2 or <20% (between field duplicate samples or readings)	0-12
Station depth - in situ	meters	± 0.5 meter	<20% between two different readers	0-15 meters

At the close of the project, the QA Manager will produce a report detailing how the resulting dataset compares with the monitoring program's data quality objectives. This review will include, for each parameter, calculation of the following:

- Percent of samples exceeding Accuracy and Precision limits.
- Average departure from Accuracy and Precision targets.
- Overall percent of samples passing QC tests vs. number proposed in Table A7.2 (Completeness).

After reviewing these calculations and taking into consideration such factors as clusters of unacceptable data (e.g., whether certain parameters, sites, dates, volunteer teams, etc., produced poor results), the Project Manager and/or QA Manager will evaluate the overall attainment of data quality objectives and

determine what limitations to place on the use of the data, or if a revision of the data quality objectives is allowable. This finding will be included in the final Data Quality Report (see Sections A9 and D2).

## **A8 Training Requirements**

Training on all aspects of project data collection and management will be provided to project participants and will be documented—including trainer(s), dates of training, and subject matter—in a Training Log (sample attached).

All members of the project team will be required to attend training/workshops appropriate to the type of monitoring they will conduct. The Field Coordinator shall ensure that volunteers receive appropriate training by organizing and conducting workshops (securing the services of expert trainers as needed) and/or arranging for volunteers to be trained at workshops held by other qualified personnel or organizations. All volunteers will receive annual refresher training refreshers following their initial training.

Names of all training participants will be documented on a Training Check-in Form (attached), with documentation in a final report.

The Field Coordinator will enter training data into the project database and records the following information: subject matter (i.e., what type of monitoring and procedures are covered), training course title, type of training materials, date and agenda, name and qualification of trainers, and names of participants trained. Volunteers shall be trained in monitoring protocols and be able to document pertinent environmental data for the evaluation site.

## **A9 Documentation and Records**

### **A9.1 Documentation**

Initially, all data will be recorded onto paper data forms. All data collection notes will be made in permanent ink, initialed, and dated, and no erasures or obliterations will be made. Completed Field Data Forms, Sampling Logs, or other types of hand-entered data will be signed and dated by the individual entering the data. Data will be subsequently recorded electronically onto computer storage media. Direct-entry and electronic data entries will indicate the person collecting or entering the data as shown in the Data Entry QC Check Form (attached). Secondary data used will be documented in the Secondary Data Form, attached. The table below details record handling procedures for this project, including the content of the final Data Quality Report (also see Section D2).

**Table A9.1. Record Handling Procedures**

<b>Activity</b>	<b>Details</b>
Document Control	The Field and Project Manager will ensure volunteers are trained on filling in the forms and data collection methods. The Field and Project Manager will be responsible for maintaining field forms. All data will be submitted from the SMAST laboratory to the Field and Project Manager upon completion of analysis - this includes the data submitted on the field forms.

Activity	Details
Data Generation	<p>Field Data Forms will be filled out by sampling volunteers/staff and submitted to the School of Marine Science and Technology Laboratory as part of the Chain of Custody form. A copy is retained and given to the Project Manager prior to submitting the field form and samples to the laboratory. The Laboratory Manager will input the field data form information into an excel spreadsheet with the results of the analytical data analyzed by the laboratory. The Data Manager/Laboratory Manager will submit results to the Project Manager on a yearly basis following the field data collection season.</p> <p>The Project Manager will label all bottles appropriately and affix the appropriate field data and chain of custody forms for the volunteers. This will ensure consistency and lack of error during the sampling event.</p>
Data Quality Report	<p>The Project Manager will submit the data package to MassDEP with any pertaining information and data evaluation narrative. The data package will include the spreadsheet with field and analytical results noting the Site Location, Sample Depth and all applicable data collected. The data evaluation summary will detail how the resulting dataset compares with the program's data quality objectives.</p>
Reporting Format	<p>The Data package will be delivered in excel format.</p>
Records Storage	<p>Records will be stored by the Project Manager at the Town of Plymouth and are available as public record. The data is also updated each year on the Town of Plymouth's Ponds and Rivers website.</p>

## A9.2 Field Records

Data Forms will provide the primary means of recording the data collection activities performed during the sampling surveys. Entries will be described in as much detail as possible so that events occurring the survey can readily be reconstructed after the fact. At the beginning of each survey, the date, start time, weather, and names of all sampling team members present will be entered, along with information about the samples, on a Field Data Form. Forms to be used for this project are listed in the table(s) below; samples are attached.

**Table A9.2. Project-Specific Datasheets and Forms for All QAPPs**

Form Name	Description
Field Data Sheet: <i>in situ</i> WQ parameters, Site conditions and Chain of Custody form as one form	Records field measurement (e.g. YSI) and sample collection info, site location and ID, crew names,

Form Name	Description
	weather conditions, etc. Accompanies samples from collection sites to lab(s).
Laboratory Data	Documents lab results; include lab SOP number, data analysis, QA/QC and results.
Training Log	Compiles information on trainings offered
Instrument Calibration Log	Documents maintenance, pre- and post-field sampling calibration and testing of equipment
Water Quality Sample Collection Log	Maintains a list of water quality samples collected in the field.

Field sheets for all samples will include:

- Station name and/or ID number
- Replicate number
- Time and date of sample collection
- Sample description (color, texture, etc.)
- Samplers' initials
- Requested analyses
- Location (the geographic location where a sample is collected)

Supplementary data for every station sampled will be recorded in the comments section of the Field Sheets. Additional data may include notes on sampling difficulties, currents, and numbers and sizes of jars used for each sample.

## Section B. Fresh Water/Water Quality Data Generation and Acquisition

### B1 Sampling Design

Trained volunteers and Town Staff will be collecting grab samples, water quality profiles pertaining to dissolved oxygen/temperature, clarity and additional field indicators. The monitoring season is April thru October. For Great Herring Pond grab samples, profiles, clarity and cyanobacteria will be collected monthly April thru October. For all other ponds - profiles and clarity will be collected monthly with grab samples collected once in the time period of mid August thru September when the water quality is anticipated to be at its poorest health.

#### B1.1 Sampling Site Selection

Monitoring locations include stations upstream and downstream of the source, as well as reference stations. Sites selected are in an area where reasonable opportunity for mixing of the effluent has occurred. Where a mixing zone has been defined in a license for discharge, sampling will be conducted immediately downstream of it. In cases where the effluent plume channels down one bank for great distances (>1 km), or where localized effluent impact is expected to be severe for a distance beyond the zone of initial dilution, sampling locations are upstream of the source, one or more in the plume, and at least two farther downstream. Monitoring locations have been selected to ensure that the physical characteristics among sites are similar, and are representative of the stream reach. Reference sampling sites are minimally impaired, and located in the same ecoregion, size class, and stream type (width, depth, gradient). Site assessment forms (sample attached) will be completed for each location.

#### B1.1 Sample Site Selection

Routine sampling activities will consist of collecting in-stream samples. Routine sampling is expected to be representative of overall water quality and sites are relatively unchanging over time to allow comparison to past and future investigations. Sites were selected at the downstream ends and/or key segmentation points of major tributaries, and at or near locations where there is a longstanding data record. Site assessment forms (sample attached) will be completed for each location.

#### B1.2 Location

See Section A6 for a description of the sampling locations. A map is attached.

#### B1.3 Sample Collection Methods

Samples will be collected via grab sampling and direct measurements using electronic instruments in the field. The details of the sampling design are described in the table below.

**Table B1.1. Freshwater Quality Field Sampling Summary**

Location ID	Parameter - Method	Frequency
Bloody Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Bloody Pond	Station depth - in situ	Monthly

Location ID	Parameter - Method	Frequency
Bloody Pond	Temperature - multi-parameter probe meter	Monthly
Bloody Pond	Phaeophytin a	Once per season
Bloody Pond	Total Nitrogen	Once per season
Bloody Pond	Total Phosphorus	Once per season
Bloody Pond	Chlorophyll-a	Once per season
Bloody Pond	Alkalinity	Once per season
Clear Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Clear Pond	Station depth - in situ	Monthly
Clear Pond	Temperature - multi-parameter probe meter	Monthly
Clear Pond	Phaeophytin a	Once per season
Clear Pond	Total Nitrogen	Once per season
Clear Pond	Total Phosphorus	Once per season
Clear Pond	Chlorophyll-a	Once per season
Clear Pond	Alkalinity	Once per season
Gallows Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Gallows Pond	Station depth - in situ	Monthly
Gallows Pond	Temperature - multi-parameter probe meter	Monthly

Location ID	Parameter - Method	Frequency
Gallows Pond	Phaeophytin a	Once per season
Gallows Pond	Total Nitrogen	Once per season
Gallows Pond	Total Phosphorus	Once per season
Gallows Pond	Chlorophyll-a	Once per season
Gallows Pond	Alkalinity	Once per season
Great Herring Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Great Herring Pond	Station depth - in situ	Monthly
Great Herring Pond	Temperature - multi-parameter probe meter	Monthly
Great Herring Pond	Phaeophytin a	Monthly
Great Herring Pond	Total Nitrogen	Monthly
Great Herring Pond	Total Phosphorus	Monthly
Great Herring Pond	Chlorophyll-a	Monthly
Great Herring Pond	Alkalinity	Monthly
Halfway Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Halfway Pond	Station depth - in situ	Monthly
Halfway Pond	Temperature - multi-parameter probe meter	Monthly
Halfway Pond	Phaeophytin a	Once per season

Location ID	Parameter - Method	Frequency
Halfway Pond	Total Nitrogen	Once per season
Halfway Pond	Total Phosphorus	Once per season
Halfway Pond	Chlorophyll-a	Once per season
Halfway Pond	Alkalinity	Once per season
Little Herring Pond	Dissolved oxygen - multi-parameter probe meter	Once per season
Little Herring Pond	Station depth - in situ	Once per season
Little Herring Pond	Temperature - multi-parameter probe meter	Once per season
Little Herring Pond	Phaeophytin a	Once per season
Little Herring Pond	Total Nitrogen	Once per season
Little Herring Pond	Total Phosphorus	Once per season
Little Herring Pond	Chlorophyll-a	Once per season
Little Herring Pond	Alkalinity	Once per season
Little Long Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Little Long Pond	Station depth - in situ	Monthly
Little Long Pond	Temperature - multi-parameter probe meter	Monthly
Little Long Pond	Phaeophytin a	Once per season
Little Long Pond	Total Nitrogen	Once per season

Location ID	Parameter - Method	Frequency
Little Long Pond	Total Phosphorus	Once per season
Little Long Pond	Chlorophyll-a	Once per season
Little Long Pond	Alkalinity	Once per season
Long Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Long Pond	Station depth - in situ	Monthly
Long Pond	Temperature - multi-parameter probe meter	Monthly
Long Pond	Phaeophytin a	Once per season
Long Pond	Total Nitrogen	Once per season
Long Pond	Total Phosphorus	Once per season
Long Pond	Chlorophyll-a	Once per season
Long Pond	Alkalinity	Once per season
Round Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Round Pond	Station depth - in situ	Monthly
Round Pond	Temperature - multi-parameter probe meter	Monthly
Round Pond	Phaeophytin a	Once per season
Round Pond	Total Nitrogen	Once per season
Round Pond	Total Phosphorus	Once per season

Location ID	Parameter - Method	Frequency
Round Pond	Chlorophyll-a	Once per season
Round Pond	Alkalinity	Once per season
Savery Pond	Dissolved oxygen - multi-parameter probe meter	Monthly
Savery Pond	Station depth - in situ	Monthly
Savery Pond	Temperature - multi-parameter probe meter	Monthly
Savery Pond	Phaeophytin a	Monthly
Savery Pond	Total Nitrogen	Monthly
Savery Pond	Total Phosphorus	Monthly
Savery Pond	Chlorophyll-a	Monthly
Savery Pond	Alkalinity	Monthly

## B2 Sampling Methods: Sample Collection and Storage

The table below summarizes sample collection and storage for parameters included in this monitoring program. Standard Operating Procedures (SOPs) for sample collection and storage are attached.

**Table B2.1. Equipment Preparation, Sample Processing, and Storage Requirements**

Parameter - Method	Sample collection method	Container Type and Preparation	Minimum Sample Quantity	Sample Preservation	Maximum Holding Time
Temperature - multi-parameter probe meter	Multi-parameter unit	-	-	-	-
Dissolved oxygen - multi-parameter probe meter	Multi-parameter unit	-	-	-	-

Parameter - Method	Sample collection method	Container Type and Preparation	Minimum Sample Quantity	Sample Preservation	Maximum Holding Time
Station depth - in situ	Depth finder unit	-	-	-	-
Chlorophyll <i>a</i> / Phaeophytin <i>a</i> Alkalinity pH	Niskon Deep Sampler	Amber	1L	Pre-cleaned acid wash	24hrs 24hrs 6hrs 6hrs
Total Nitrogen	Niskon Deep Sampler	Plastic	250 mL	-	Frozen 60 days
Total Phosphorus	Niskon Deep Sampler	Plastic	250 mL	-	Frozen 60 days

\*Pre-cleaned – acid washed with 10% HCL

\*\**in situ*: single and/or multiple probe

## B2.1 Water Quality Monitoring

### ***Equipment/Instrument Calibration***

Multi-parameter or individual sensors will be calibrated both prior to and following field use in accordance with the manufacturer's instruction manual as described in Sections B7.1 and B7.2. If no instructions specific to the instrument are available, general calibration methods as described in the Field Operations Manual will be followed and documented on an Instrument Calibration Log (sample attached).

### ***Multi-Parameter Unit Deployment***

*In situ* measurements will be made using a calibrated water quality multi-parameter unit at each station. Measurement of temperature, conductivity, dissolved oxygen, and pH will be taken at surface at riverine sites; at lake sampling sites deeper than 2m, a hydrographic profile will be obtained. Measurements will be collected as the multi-parameter unit is lowered down to 0.5 m from the bottom. A Water Quality Sample Collection Log and Field Data Form for *in situ* WQ Parameters will be completed for each monitoring location (samples attached).

## B3 Sample Handling and Custody

The attached SOPs describe handling of samples while in the field, including storage requirements.

Labels with the following information will be attached to sample containers:

- Sample number
- Site ID
- Time and date of collection

- Preservation requirements
- Name of sampler and organization

Samples for shipment will be prepared as follows:

- All samples will be appropriately preserved and packaged for transport.
- If obtainable samples are missing, the Project Manager and Field Coordinator will determine corrective action (e.g., reschedule a site visit or return to the site that same day to complete collection of the missing samples).
- All samples will be labeled and the labels checked for completeness, legibility, accuracy, and consistency.
- Labels and forms will be reviewed to ensure consistent sample ID information.
- Each sample container will be inspected to make sure there are no leaks and that all containers are properly sealed.

The Field Coordinator will complete the Chain of Custody Form(s) for samples shipped to a laboratory. Copies of custody forms will be made and retained by the team. The original form will be sent in the container with the sample. Copies of all custody forms will be included in the coolers when the Field Coordinator sends samples to the labs. Sample labels and Chain of Custody Forms are attached.

## B4 Analytical Methods

*In situ* parameters measured by calibrated sensors on site, including temperature, dissolved oxygen, conductivity, pH and turbidity, do not require analytical methods. Laboratory analysis of discrete samples to be conducted are indicated in the table below.

**Table B4.1. Approved Analytical Methods**

CSP/SMAST Analyte Details for Plymouth PALS Snapshot Ponds Monitoring Program and Plymouth Pond and Lake Diagnostic Assessments								
Analyte	units	Minimum Detection Limit	Accuracy/Precision	Analysis Method/Type	Max Holding Time	Lab Duplicates	Lab Blanks	Lab Spikes
Alkalinity	mg/l as CaCO <sub>3</sub>	0.5	80-120% Std. Value	Acid Titration <sup>1</sup>	6 hrs	10%	5%	5%
Chlorophyll <i>a</i> /Phaeophytin <i>a</i>	µg/l	0.1	80-120% Std. Value	Acetone extraction <sup>2</sup>	24 hrs	5%	5% + after any sample off scale	5/day minimum
Nitrogen, Total	µM	0.06	80-120% Std. Value	Persulfate digestion <sup>3</sup>	Frozen 60 days	10%	2/sample set	10%
pH	stnd units	NA	±0.2 of QC standard	Electrode <sup>4</sup>	6 hrs	10%	5%	5%

Phosphorus, Total	µM	0.1	80-120% Std. Value	Persulfate digestion <sup>5</sup>	Preserved 60 days	5/sample set	5% + after any sample off scale	5/day minimum
Notes:								
<p>a) Accuracy is determined by the analysis of spiked samples and comparison to known standards, except as noted in the table. QC sample recoveries may also be used to assess accuracy when spiked sample analysis is not possible. The general data quality observation for all analyte blanks are no exceedances of the MDL. All procedures, methods, and lab SOPs are documented in the SMAST Coastal Systems Analytical Facility Laboratory Quality Assurance Plan (2014)</p> <p>b) For accuracy determination, comparison of spike samples and known standards is preferred.</p> <p>c) Overall precision is measured using the Relative Percent Difference, RPD (or std. deviation for <math>n &gt; 2</math>) of field duplicate samples. Lab precision is based on an estimate of the RPD between duplicate aliquots of the same lab sample.</p> <p>d) Diagnostic assessments that do not utilize the CSP/SMAST Coastal Systems Analytical Facility Laboratory will need to utilize approved methods that attain the minimum listed detection limits.</p> <p>e) Lab duplicates, blanks, and spikes are based on assay SOPs (see attached in Appendix F)</p>								

#### 1. Methods details:

- 1) Standard Methods 19th Edition, Method 2320-B
- 2) Parsons, T.R., Y. Maita and C. Lalli. 1989. Manual of Chemical and Biological Methods for seawater analysis. Pergamon Press, 173 pp. Analysis using Turner Designs - AU-10.
- 3) Standard Methods 19<sup>th</sup> Edition, Method 4500-Norg-D D'Elia, C.F., P.A. Steudler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22:760-764.
- 4) Standard Methods 19th Edition, Method 4500-H+B
- 5) Standard Methods 19th Edition, Method 4500-P-B.5, persulfate digestion and assay as orthophosphate.

## B5 Field and Analytical Laboratory Quality Control

The monitoring project will include appropriate field and laboratory QC samples to assess general data quality issues, as well as specific data quality objectives. The following sections, including summary tables, describe QC measures to be undertaken.

### B5.1 Field Duplicates and Field Blanks

Duplicates for lab analysis will be collected side by side and simultaneously with samples. Field blanks will be carried and stored alongside field samples. Field duplicates and field blanks will be submitted to the laboratory along with all other samples for analysis. Parameters measured using a meter will also be subject to duplicates and blanks.

Field duplicates and field blanks for each parameter will be taken for 10% of all water quality samples taken per sampling event, for a total of 20% QC samples per parameter per sampling event. Sampling crews will be assigned collection of field duplicates and blanks on a rotating basis to monitor practices of each crew over the course of a sampling season/year.

**Table B5.1. Quality Control Measures**

Parameter - Method	Frequency of Sampling	Number of samples per sampling event	Precision Check: Field duplicates per sampling event	Accuracy Check: Field blanks per sampling event	Precision Check: Lab duplicates per sampling event	Accuracy Check: Lab blanks per sampling event	Precision Check: Lab spikes per sampling event
Dissolved oxygen - multi-parameter probe meter	Monthly	9	10%	NA	NA	NA	NA
Station depth - in situ	Monthly	9	10%	NA	NA	NA	NA
Temperature - multi-parameter probe meter	Monthly	9	10%	NA	NA	NA	NA
Phaeophytin a	Once per season	8	10%	10%	5%	5%	5/day minimum
Total Nitrogen	Once per season	8	10%	10%	10%	2/sample set	10%
Total Phosphorus	Once per season	8	10%	10%	5/sample set	5%	5/day minimum
Chlorophyll-a	Once per season	8	10%	10%	5%	5%	5/day minimum
Alkalinity	Once per season	8	10%	10%	10%	5%	5%

**Table B5.2. Field Quality Control (measured using sensors)**

Parameter - Method	Check Description	Frequency	Acceptance Criteria	Corrective Actions
Temperature - multi-parameter probe meter	Verify performance of temperature probe using wet ice bath; Verify with NIST-certified thermometer	Annual; Prior to initial sampling	Functionality = $\pm$ 1.0 °C	See manufacturer's instructions
Dissolved oxygen - multi-parameter probe meter	Check DO calibration in field against atmospheric standard (ambient air saturated with water)	At the beginning and end of each day	Alignment with instrument manufacturer's specifications or $\pm$ 1.0 mg/L	AM: Re-calibrate; PM: Flag day's data. Change membrane.

**Table B5.3. Data Validation Quality Control for Water Chemistry**

Activity	Requirements and Corrective Action
Range checks, summary statistics, and/or exploratory data analysis	Current reporting errors or qualify as suspect of invalid
Review holding times	Qualify value for additional reviews
Review data from QA samples	Determine impact and possible limitations on overall data usability

## B6 Instrument/Equipment Inspection and Testing

All equipment used to collect or analyze ambient or collected samples will undergo periodic maintenance and calibration verification performed by manufacturer's representatives or service consultants. These procedures will be documented by date and the signature of person performing the inspection. (For example, multi-parameter probes will receive annual [or as needed] maintenance and calibration checks by manufacturers or certified service centers.) All other sampling gear and laboratory instrumentation will be maintained in good repair as per manufacturer's recommendations to ensure proper function. The following table lists typical procedures to be undertaken.

Records of equipment inspection, maintenance, repair, and replacement will be kept in a logbook, along with standard operating procedures for instrument maintenance and calibration.

**Table B6.1. Typical Instrument/Equipment Inspection and Testing Procedures**

Equipment	Inspection frequency	Type inspection	Maintenance, Corrective Action	Person (Role) Responsible
Nutrient sample bottles	Before each use	Visually inspected for obvious defects, damage, and contamination	Clean before use or as needed. If needed, acid wash prior to use (or clean-certified from manufacturer or lab)	Lab Coordinator and Field Coordinator
Secchi disk, calibrated line	Before each use	Visual for integrity, cleanliness	Wipe tape, spare disk, spare line	Field Coordinator
Multi-parameter units; individual sensors	Before each use	Battery life, membrane condition	Spare batteries, spare membranes	Field Coordinator
Sampling device e.g., Van Dorn	Before each use	Visual for integrity, cleanliness	Repair, replace if necessary	Field Coordinator
GPS	Before each use	Battery life	Repair; replace; spare batteries on hand	Field Coordinator

## B7 Field Equipment/Maintenance, Inspection, and Calibration

### B7.1 Pre-measurement Instrument Checks and Calibration

Field instruments will be tested and calibrated prior to sampling, either prior to departure for the site or at the site, and documented on an Instrument Calibration Log (sample attached)

Site location will be verified using a GPS receiver. Field crews will have access to backup instruments if any instruments fail the manufacturer performance tests or calibrations.

#### ***Multi-Parameter unit***

The dissolved oxygen, pH, temperature, and conductivity sensor functions of the multi-parameter unit or individual sensors will be calibrated prior to departure to the sampling site(s) as described in the following table documented on an Instrument Calibration Log (sample attached). A single calibration will be considered sufficient for the day.

**Table B7.1. Instrument Calibration Procedures**

Parameter - Method	Instrument	Type of Inspection	Inspection and Calibration Frequency	Standard of Calibration Used	Corrective Action
Temperature - multi-parameter probe meter	Multi-parameter sensor	Battery life, electrolyte, probe integrity	Before each monitoring event	Verify performance of temperature probe using wet ice	According to manufacturer's instructions
Dissolved oxygen - multi-parameter probe meter	Multi-parameter sensor	Battery life, electrolyte, probe integrity, membrane condition (DO)	Before each monitoring event	Std. solutions	According to manufacturer's instructions. DO: replace membrane or correct probe.

"External standards" refers to standards of reliable quality obtained from reputable commercial or other suppliers; "known standards" refers to those where the value is known before calibration.

## **B7.2 Post-measurement Calibration Check—Multi-Parameter unit**

After all sensor measurements have been completed for the sampling day, a post-measurement calibration check of the parameter sensor will be performed and documented on an Instrument Calibration Log (sample attached).

## **B7.3 Instrument/Equipment Inspection, Testing Procedures**

Equipment maintenance will be conducted routinely. Records of equipment inspection, maintenance, repair, and replacement will be recorded in a logbook.

## **B8 Inspection/Acceptance of Supplies and Consumables**

The Field Coordinator will be responsible for ensuring correct sample handling by:

- Ensuring availability of all required sampling supplies in the field.
- Properly labeling all sample containers for biological samples in the field.
- Recording all relevant sampling information on the Sample Collection Log, Field Sheets and Forms, and Chain of Custody Forms (samples attached).
- Coordinating the transfer of all samples from the field to laboratories for analysis.
- Delegating tasks as indicated in the table below.

**Table B8.1. Critical Field Supplies, Acceptance Criteria, and Responsibility for Critical Field Supplies**

Critical Supplies and Consumables	Inspection Requirements and Acceptance Criteria	Person (Role) Responsible
Sample containers	Visually inspected for cracks, breakage, and cleanliness. May be reused if acid washed.	Lab Coordinator
Calibration standards	Checking that the solutions are within expiration dates.	Lab Coordinator
Filters and related consumables	Check that it is not past expiry date.	Lab Coordinator

## B9 Data Acquisition Requirements

Secondary data (historical reports, maps, literature searches, and previously collected analytical data) may be used in the preparation of the sampling plan. These data may come from sources such as:

- Prior reports specific to the area.
- Results of state agency or other studies water quality monitoring data.
- Pertinent data collected by federal agencies, such as USGS bathymetry data and NOAA weather records.
- Surveys completed in the embayment or embayment system of interest, including those identified through MassBays' Inventory of Plans and Assessments (<https://www.mass.gov/service-details/massbays-inventory-of-plans-and-assessments>).

Secondary data used will be documented in the Secondary Data Table, attached, according to Sections A9 and C2.

## B10 Data Management

Data quality control steps will be taken at several stages. Documentation of data recording and handling, including all problems and corrective actions, shall be included in all preliminary and final reports (Corrective Action Reporting Form attached). See Section A9 for recording handling and storage procedures.

### B10.1 Process and Procedures

During each sampling trip, sampling volunteers will use a standardized field sheet provided by the Project Manager/Field Coordinator to record date, time, and field notes such as weather conditions samples collected, etc. The Project Manager/Field Coordinator will retain a copy of each of the field sheets. When samples are collected the field sheets are submitted as part of the chain of custody to the laboratory. The Laboratory Coordinator will then enter the field data along with the sample results into an excel spreadsheet and submitted annually to the Project Manager.

### B10.2 Data Handling

During each sampling trip, sampling volunteers will use a standardized field sheet provided by the Project Manager/Field Coordinator to record date, time, and field notes such as weather conditions samples collected, etc. This field data sheet includes the collection of temperature and dissolved oxygen recordings via a handheld multi-probe meter. The Project Manager/Field Coordinator will retain a copy

of each of the field sheets. When samples are collected the field sheets are submitted as part of the chain of custody to the laboratory. The Laboratory Coordinator will then enter the field data along with the sample results into an excel spreadsheet and submitted annually to the Project Manager.

### **B10.3 Management Requirements**

Records will be stored by the Project Manager at the Town of Plymouth and are available as public record. The data is also updated each year on the Town of Plymouth's Ponds and Rivers website. Data will be shared with MassDEP via data submission process.

## **Section C. Assessment and Oversight**

### **C1 Assessment and Response Actions**

This section identifies the number, frequency, and type of planned assessment activities that will be performed to ensure implementation of this QAPP. These activities will be overseen by the Project Manager.

#### **C1.1 Assessments**

##### ***Field Sampling Readiness Review***

A field survey plan will reference the specific field activities to be conducted and lists of equipment provided.

##### ***Field Sampling Internal Audit***

The Project Manager in coordination with the Field Coordinator will be responsible for periodic internal audits to verify that field sampling procedures and measurements are properly followed. The internal field audit checklist will include examination of the following:

- Field sampling records
- Sample collection, handling, and packaging procedures
- Adherence to the SOPs and this QAPP
- QA procedures
- Chain of custody
- Sample documentation

Results of internal field audits will be documented in QA reports to the Project Manager (Section C2).

##### ***Laboratory Audits***

The selected laboratory(ies) will participate in laboratory audits and/or Performance Evaluation studies as described in their Laboratory Quality Assurance Plan. The results of the audit, including resolution of any deficiencies, will be included in the QA reports, as described in Section C2.

##### ***Data Audits***

Data will be audited under the direction of the QA Manager as part of the data validation process (Section D1). Raw data will be reviewed for completeness and proper documentation. Errors noted in the data audits will be communicated to analyses and laboratory management and corrected data will

be verified. Audits of the data collection procedures at contracted laboratory will be the responsibilities of the laboratories. Each laboratory is fully responsible for the verification and validation of the data it submits. Data must be submitted in QAPP-prescribed formats only. All data must be reviewed by the contracted laboratories' QA Manager or designee prior to submission to the Project Manager.

## **C1.2 Assessment Findings and Corrective Action Responses**

All technical personnel share responsibilities for identifying and resolving problems encountered in the routine performance of their duties. Issues that affect the schedule, cost, or performance of project tasks will be reported to the Project Manager. The Project Manager will be accountable for overall implementation of the Project. The Project Manager will be responsible for identifying and resolving problems that (1) have not been addressed in a timely manner or successfully at a lower level, (2) influence multiple components of the projects, or (3) require consultation with contracted laboratories. The Project Manager will be responsible for evaluation of the overall impact of the problem on the project and for developing and implementing corrective actions. The Project Manager will also identify and resolve problems that may necessitate changes to this QAPP. Problems identified by the Field Coordinator and the QA Manager will be reported to the Project Manager and corrected as described in Section C2.

The QA Manager will generate and/or review all corrective actions required during the project and monitor their effectiveness in meeting project quality objectives. Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out-of-limit QC performance that can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation and assessment. All corrective action proposed and implemented should be documented in the QA reports to the Project Manager. A copy of the Corrective Action Reporting Form (template attached) will be provided as described in Section C2.

### ***Field Corrective Action***

Corrective action in the field may be needed when the sample frequency is changed (i.e., more/fewer samples, sample locations other than those specified in the Study Plan), or when sampling procedures and/or field analytical procedures require modification due to unexpected conditions. The survey crew may identify the need for corrective action. The Project Manager and QA Manager will approve the corrective measure and ensure that the survey crew implements the corrective action.

Corrective action resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. A corrective action issue which directly impacts the project DQOs will be reported to the Project Manager. Corrective action will be documented in QA reports to project management (Section C2). Corrective actions will be implemented and documented as follows:

- A description of the circumstances that initiated the corrective action
- The action taken in response
- The final resolution
- Any necessary approvals
- Effectiveness of corrective action

### ***Laboratory Corrective Action***

Corrective action in the laboratory is specified in laboratory SOPs (attached) and may occur prior to, during, and after initial analyses. If the corrective action makes it impossible to achieve project objectives, the Laboratory Manager will notify the QA Manager, who will in turn notify the Project Manager, who will determine the action to be taken.

Corrective actions will be documented in both the laboratory's corrective action files, and in the data report generated by the laboratory.

### ***Corrective Action during Data Validation and Data Assessment***

The need for corrective action may be identified during either data validation or data assessment. Potential types of corrective action may include re-sampling by the survey crew or reanalysis of samples by the laboratory. These actions are dependent upon the ability to mobilize the survey crew and whether the data to be collected are necessary to meet the required QA objectives. If the data validator or data assessor identifies a corrective action situation that impacts the achievement of the project objectives, the Project Manager will be notified.

## **C2 Reports**

Data that have passed preliminary QC analysis (Section B5) will be uploaded to WQX and shared with interested audience. Any data uploaded or released will be accompanied by the caveat that they are for review purposes only and subject to correction after completion of a full data review at the end of the sampling season.

The Project Manager will prepare a final report which will be shared with the QAPP distribution list. The final report will include tables and graphs developed for initial data distribution efforts and will describe the program goals, methods, quality control results, data interpretation, and recommendations and include:

- Raw data
- QC data
- Secondary data used
- Associated metadata
- Questionable data flagged
- Preliminary or final report
- Other reports or supporting documentation deemed relevant by the Project Manager

## Section D. Data Review and Usability

### D1 Data Review and Validation

A review protocol is developed to ensure that data validation and verification is conducted in an objective and consistent manner. The review will include the required number, frequency and types of assessments (peer reviews, management systems reviews, technical systems audits, performance evaluations, and data quality reviews), and names of staff responsible for this task.

#### ***Field Data***

The field data verification includes verification of sampling design, sample collection procedures, and sample handling. Field data will be reviewed regularly by the Data Manager to ensure that the records are complete, accurate, and legible and to verify that the sampling procedures are in accordance with the protocols specified in the QAPP (refer to Section D2.1 for the specific elements reviewed).

#### ***Laboratory Data***

Prior to the release of any data from a contracted laboratory, the data will be reviewed and approved by laboratory personnel. The review will consist of a tiered approach (Section D2.2) that will include reviews by the person performing the work, by a qualified peer, and by supervisory and/or QA personnel.

#### ***Data Management***

The review process will include verification of manually entered data and QC checks run in a software application prior to submitting the data to WQX. Detailed descriptions of these processes are included in Sections B10 and D2.

### D2 Verification and Validation Methods

Data verification methods will ensure that the reported results reflect what was actually done and document that the data fulfill applicable requirements. Validation will further identify and evaluate the impact of any technical non-compliance or quality control non-conformance on the complete data set.

#### ***Field Data***

Field records will be reviewed by the Project Manager to ensure that:

- Logbooks and standardized forms have been filled out completely and that the information recorded accurately reflects the activities that were performed.
- Records are legible and in accordance with good recordkeeping practices, i.e., entries are signed and dated, data are not obliterated, changes are initialed, dated, and explained.
- Equipment calibration, sample collection, handling, preservation, storage, and shipping procedures were conducted in accordance with the protocols described in this QAPP, and that any deviations were documented and approved.
- DQIs are calculated as described in Section D3 and results compared with Acceptance Criteria/Performance Goals (detailed in Section A7) for review by the QA Manager; data compare well to historic data or its “reasonableness.”

### ***Laboratory Data***

As a part of data validation, contracted laboratories will ensure that:

- The QC checks specified in Sections A7 and B5 were conducted and met the acceptance criteria.
- All data that are hand-entered (i.e., typed) will be 100% validated prior to use in calculations or submission to the Project Manager.
- All manual calculations will be performed by a second staff member to verify that calculations are accurate and appropriate.
- Calculations performed by software will be independently verified at a frequency sufficient to ensure that the formulas are correct, appropriate, and consistent, and that calculations are accurately reported.

Once data have been generated and compiled in the laboratory, laboratory personnel will review the data to identify and make professional judgments about any suspicious values. All data found not to meet QC standards will be flagged and maintained, but excluded from reporting to DEP. These data may not be used in calculations or data summaries. No data measurements will be eliminated from the data set and data gaps will never be filled with other existing data. The loss of any samples during shipment or analysis will be noted in the data set.

### ***Data Management***

Laboratory data will be reviewed by the Data Manager prior to the electronic submission to WQX. Data review may include methods such as plots, logical checks, and range checks to identify suspect values. All data found not to meet QC standards will be coded as "Rejected" in the "Result Status ID" field for WQX submissions. Routine system back-ups should be performed regularly. Detailed description of data management and review is provided in section B10 of this QAPP.

### ***Project Deliverables***

Upon completion of the verification/validation process, a dataset packet will be prepared for submittal to WQX. The data will be in the format prescribed for submission to WQX. This documentation will include the following elements (see Section A9):

- Cover letter that includes a description of any problems.
- List of problems encountered, and corrective action taken.
- List of samples/images planned versus collected, or measurements planned versus reported.
- Quality Assurance Statement including a checklist of QA actions, and notes on deviations and corrective actions.
- Table(s) of data submitted.

## **D3 Reconciliation with User Requirements**

This section describes how the verified/validated project data will reconcile with the project DQOs, how data quality issues will be addressed, and how limitations on the use of the data will be reported and handled. To meet these DQOs, a combination of qualitative evaluations and statistical procedures will be used to check the quality of the data. These procedures will be used by the laboratory generating the data, and by the Project Manager or a designee.

The data generated must meet the project DQOs defined in Section A7 of this QAPP. The primary objectives for assessing the usability of the data are to ensure that (1) data denote conditions and habitat quality in the area being studied, (2) all datasets are complete and defensible, and (3) data are of the quality needed to meet the overall objectives of the program.

### **D3.1 Comparison to Measurement Criteria**

#### ***Accuracy and Precision Assessment***

The accuracy and precision of the data generated during this project will be assessed by comparison to the DQOs specified in Table A7.2. Comparison of laboratory control samples will provide accuracy assessments. Relative Percent Difference (RPD) between duplicates will represent precision, and is defined by the following equation:

$$RPD = \frac{|X_1 - X_2|}{(X_1 + X_2)/2} * 100$$

*where*

RPD = Relative Percent Difference (as %)

$|X_1 - X_2|$  = Absolute value (always positive) of  $X_1 - X_2$

$X_1$  = Original sample concentration

$X_2$  = Duplicate sample concentration

Data that fail to meet the data quality criteria may necessitate sample reprocessing, analysis of archival material, sample recollection, or flagging of the data, depending on the magnitude of the nonconformance, logistical constraints, schedule, and cost.

#### ***Representativeness Assessment***

Representativeness of the field data will be assessed by verifying that the sampling program was implemented as proposed and that proper sampling techniques were used. The assessment of representativeness in the laboratory will consist of verifying that the proper analytical procedures and appropriate methods were used.

#### ***Completeness Assessment***

Completeness is the ratio of the number of valid sample results to the total number of results planned for collection. The overall completeness goal for the monitoring program is 80% of planned samples to be collected and analyzed. The Project Manager will assess the completeness of the overall data generation against the project goals. Following completion of the sampling, analysis, and data review, the percent completeness will be calculated and compared to the project objectives stated in Table A7 using the following equation:

$$\%C = \frac{N}{T} * 100$$

*where*

$\%C$  = Completeness (as %)

$N$  = Number of usable results

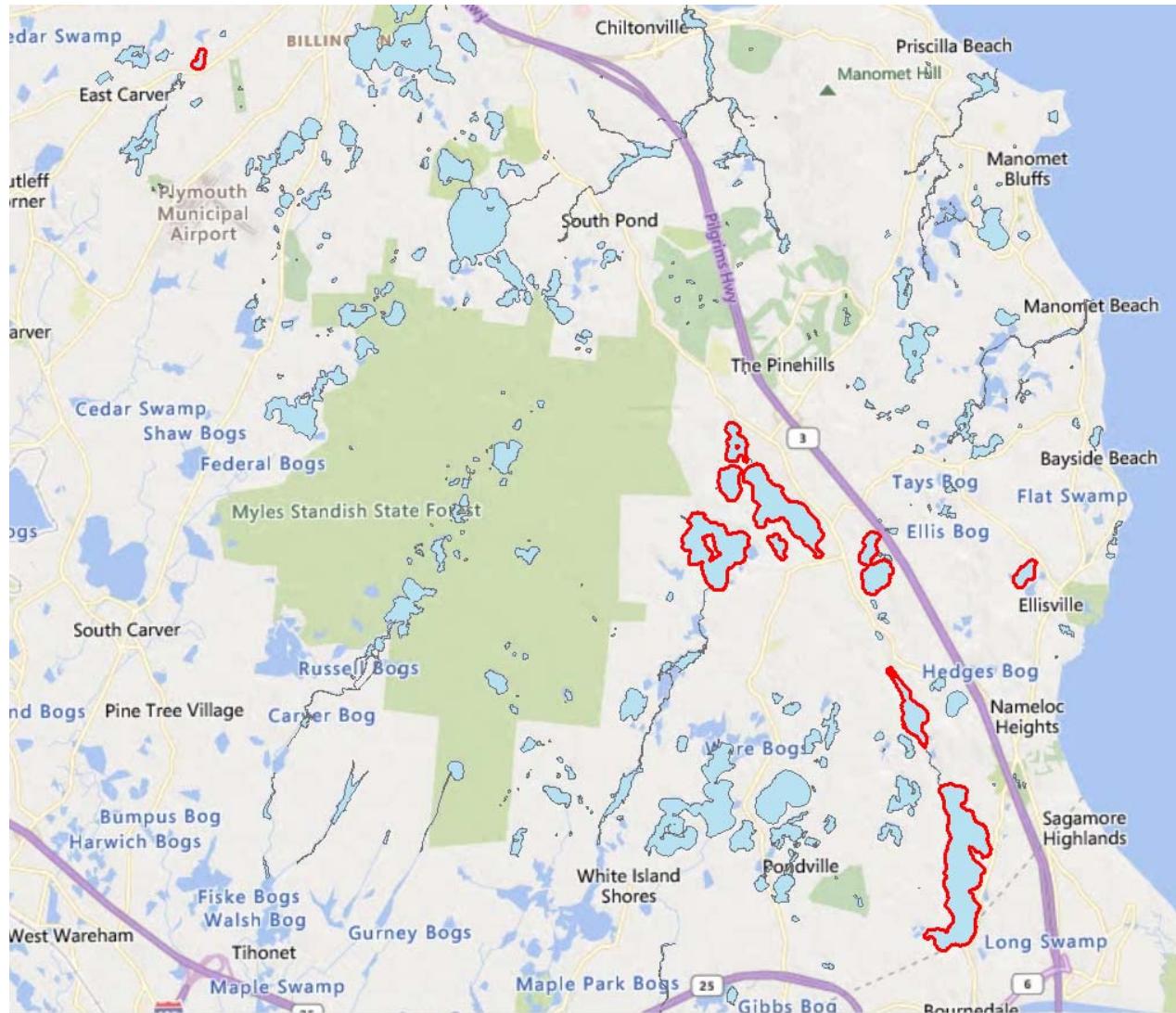
$T$  = Targeted number of samples planned to be collected

If the goal is not met, data gaps will require evaluation to determine the effect on the intended use of the data. Sample re-analysis, analysis of archived material, and/or re-collection of the sample may be appropriate depending on criticalness of the missing data, logistical constraints, cost, and schedule.

### **D3.2 Overall Assessment of Environmental Data**

Data assessment will involve an evaluation to determine if the data collected are of the appropriate quality, quantity, and representativeness for the purposes required by project as well as for submission to WQX. This evaluation will be performed by the Program Manager in concert with other users of the data. Data generated in association with QC results that meet these objectives will be considered usable. Data that do not meet the objectives and/or the data validation criteria might still be usable. This assessment may require various statistical procedures to establish outliers, correlations between data sets, adequate sampling location coverage, etc., in order to assess the effect of qualification or rejection of data. The effect of the qualification of data or loss of data deemed unacceptable for use, for whatever reason, will be discussed and decisions made on corrective action for potential data gaps.

## ATTACHMENT A: Map(s) of Sampling Locations



## **ATTACHMENT B: Sample Collection and Storage SOPs**

All sampling processes begin the day before field sample collection, by ensuring all required instruments and supplies are gathered. The Field Coordinator will supply sample bottles and chain of custody/data sheets required for each event. Sample bottles, including bottles for QA/QC duplicates, ice packs, coolers, and meters will be supplied by the Field Coordinator. Bottles will be acid-leached, 1L, dark Nalgene bottles by the Lab Coordinator.

In the field, the PALS Snapshot sampling location or diagnostic sampling location is determined by review of available bathymetric maps or measurement of water depth from acoustic depth sounder or Secchi disk. If GPS coordinates are available for the sampling location, these are used to find the sampling location and, if an in-pond sampling site, a depth reading is collected and compared to past depth recordings to confirm the site. The location and time of sampling is recorded on the Plymouth PALS Ponds Sampling Sheet for all PALS Snapshot samplings.

The following describes PALS Snapshot samplings:

- A Secchi clarity reading is collected by lowering the Secchi disk over the shaded side of the boat, recording the depth of just disappearing based on visual inspection, recording the depth of just reappearing as the disk is brought back to the surface, and averaging the two readings for the final Secchi depth. All readings are recorded on the sampling sheet. Total depth is determined by acoustic depth sounder or when necessary gently lowering the Secchi disk to the bottom of the pond and recording the depth.
- After the Secchi readings are recorded, the DO meter is used to record dissolved oxygen (in mg/L) and temperature (in °C) at 0.5 m, 1 m, 2 m, and other 1 m increments to within a minimum of 0.5 m of the bottom. Depending on the meter used, volunteers will be trained to lightly bob the probe cable to facilitate reading stabilization. If duplicate readings are being collected, readings will be collected from the deepest depth to the shallowest depth at the same depths as during the initial readings.
- Water samples are then collected at depths based on the total depth. At each pond, one sample each is collected at depths of 0.5 m and 1 m off the bottom. If the pond is ~9 m deep, one additional sample is collected at a 3 m depth, so a total of three samples are collected at the pond at depths of 0.5 m, 3 m, and 1 m off the bottom. If the pond is greater than 11 m deep, one additional sample is collected at 9 m, so a total of four samples are collected at the pond at depths of 0.5 m, 3 m, 9 m, and 1 m off the bottom. A minimum of two samples is collected from each pond. Samples are collected via a 2.2 L Niskin Sampler designed to collect discrete samples at specified depth. Visual inspection of deep water sample is conducted to ensure that no obvious sediment is included; if sediment is found, sample is discarded, device is rinsed, and another sample is collected. Filling of the water bottles is done in such a way that the fill tube from the device does not touch the water bottle during the water transfer. After filling, the bottles are transferred to a cooler and stored with ice packs sufficient to allow the water samples to attain 4°C. At the end of the sampling day, coolers and enclosed samples are returned to the laboratory.

At the CSP/SMAST Coastal Systems Analytical Facility Laboratory, all samples are transferred to a 4°C cooler after logging them in. Water samples are divided into appropriate aliquots for the laboratory analytes. Total Phosphorus aliquots are preserved with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and stored in laboratory refrigerators at 4°C, while total nitrogen aliquots were frozen (-22°C). Pigment aliquots are filtered within 6 hours of sampling and extracts are stored in laboratory freezers at -22°C.

**ATTACHMENT C: Forms**



**POND AND LAKE SAMPLING DATA SHEET**  
Plymouth Pond and Lake Stewardship (PALS) Monitoring Program

LAKE/POND NAME:

Sample Collector(s): \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_ (AM or PM)

**Observations (write in or circle as appropriate):**

Water Color \_\_\_\_\_ (blue, brown, green, blue/green, red/orange, white, etc)

**Weather (circle):** 1. Cloudless, 2. Pt. Cloudy, 3 Overcast, 4. Rain, 5. Fog/Haze, 6. Drizzle, 7. Intermittent Rain

Wind (circle): 1. Calm. 2. Light Breeze. 3. Steady Wind. 4. Strong Wind

<u>Weather (circle):</u> 1. Cloudless, 2. Pt. Cloudy, 3 Overcast, 4. Rain, 5. Fog/Haze, 6. Drizzle, 7. Intermit. Rain
<u>Wind (circle):</u> 1. Calm, 2. Light Breeze, 3. Steady Wind, 4. Strong Wind
<b>Plants on Pond (check conditions):</b>
Waterlilies coverage of pond surface:
Floating Algae on pond surface:
Emergent Grasses/Sedges of surface:
Other plant #1_____:
Other plant #2_____:
Other Notes:

TOTAL DEPTH: \_\_\_\_\_ meter

**SECCHI READING:** Disappearing: \_\_\_\_\_ meter      Reappearing: \_\_\_\_\_ meter

### GPS Coordinate:

DISSOLVED OXYGEN/TEMPERATURE PROFILE      Meter Calibrated? YES    NO

Meter Manufacturer: \_\_\_\_\_ Model# \_\_\_\_\_

Record DO/Temp profile in one-meter increments except for the first surface reading which is taken at 0.5 m (for example: 0.5 m, 1 m, 2 m, 3 m, etc.). If the pond is very shallow (3 meters or less), record readings at 0.5 meter increments (for example: 0.5 m, 1 m, 1.5 m, 2 m, etc.).

LAKE/POND NAME: \_\_\_\_\_

Sample Collector: \_\_\_\_\_ Date: \_\_\_\_\_

WATER QUALITY SAMPLING

**LIST TOWN, POND NAME, SAMPLE DEPTH, AND DATE ON BOTTLE LABEL**

<b>⇒ POND GREATER THAN 9 METERS DEEP ⇐</b>			
Sampling Depth	Bottle Label (Town, Pond Name, Sample Depth, Date & Time)		
a. just below the surface	Date:	Time:	
b. 3 m down	Date:	Time:	
c. 9 m down	Date:	Time:	
d. 1 m above the bottom	Date:	Time:	

**⇒ In ponds ~9 m deep, collect three samples  
(just below the surface, 3 m down, and 1 m above the bottom).**

<b>⇒ POND LESS THAN 9 METERS DEEP ⇐</b>			
Sampling Depth	Bottle Label (Town, Pond Name, Sample Depth, Date & Time)		
a. just below the surface	Date:	Time:	
b. 1 m above the bottom	Date:	Time:	

**⇒ In ponds approximately 1 m deep, please collect two samples just below the surface.**

---

TIME SAMPLING COMPLETED: \_\_\_\_\_ (AM or PM)

All water samples must be kept cold, in a cooler with ice packs.

**SAMPLES MUST BE DROPPED OFF TO LAB BY 2:30PM MON-THURS (NO HOLIDAYS). IF COORDINATED PRIOR WITH LAB, MAY BE DROPPED OFF A LOCKER AT STATE POLICE BARRACKS BOURNE ROTARY (2014 code) MON-WED.**

**SAMPLE SIGNOFFS**

	Signature	Received	Delivered
		Date/Time	Date/Time
Pond Sampler/Town			
Lab			

# COASTAL SYSTEMS GROUP

## Chain of Custody Record



## Equipment Log

## Instrument Calibration Log and Maintenance

## POND SCHEDULE 2023 - Spring 2024

### Great Herring Pond (Kim Lab and assist as needed)

#### 6 deep sampling 0.5, 3M, 8,9, 10 and

	April	9	Dup
	May	9	Dup
	June	9	Dup
	July	9	Dup
	August	9	Dup
	Sept	9	Dup
	October	9	Dup
	April (2024)	9	Dup
	May (2024)	9	Dup
	June (2024)	9	Dup

### Little Herring Pond

	Aug	2	

### Savery Pond (Paula and Kim to Lab)

	June	2	
	July	2	
	August	2	
	Sept	2	

### Clear Pond (Kim to lab)

	August	2	

### Six Ponds (Kim to lab)

	August	15	

Long 4, Round 2, Halfway 2, Little Long 2, Gallows 3, Bloody 2

117 Need 10 duplicates (105)

## ATTACHMENT D: Laboratory SOPs and QAPP

### Coastal Systems Analytical Facility Laboratory SOP: Total Nitrogen/Total Dissolved Nitrogen

Revised: 15-Nov-02 (DSW & BLH)

#### **Introduction:**

Total nitrogen/total dissolved nitrogen in natural waters is analyzed by persulfate digestion as modified from Lachat Instruments Division of Zellweger Analytics Inc. Samples for total dissolved nitrogen are filtered through a 0.45  $\mu$ m membrane filter. Both filtered and unfiltered samples can be oxidized to nitrate and then analyzed using the nitrate/nitrite method described in this manual.

#### **Equipment:**

Autoclave

Autoclavable 25 x 125 mm screw cap test tubes

1 liter class A Volumetric Flasks

Transfer Pipettes (disposable), 10-25 ml

Adjustable Eppendorf Pipettes, 100-1000  $\mu$ L

#### **Consumable Supplies:**

Potassium persulfate  $K_2S_2O_8$  (Fisher Number P282-500)

Sulfuric Acid  $H_2SO_4$  (Fisher Number A300-212)

Potassium Nitrate  $KNO_3$  (Fisher Number P263-500)

#### **Preparation of Samples**

In a labeled, acid-washed, autoclavable 25 x 125 mm screw cap test tube add 5 ml of sample, which has been pre-filtered through a 0.22  $\mu$ m membrane filter, or standard, and 7.5 ml of the persulfate oxidizer.

Tighten cap and autoclave at 110° C for 50 minutes.

After autoclaving, add 1.0 ml of the Boric Acid Buffer, 0.75 mls of 0.3 N HCl and 0.75 mls of MilliQ to each test tube. Shake each test tube and assay for Nitrate+Nitrite following the Lachat Auto-analyzer SOP.

#### **Data Calculations**

Determine column correction factor by averaging the standards run on the Lachat instrument. Multiply column correction by the raw value of the sample determined by the Lachat. Subtract from the result 2/3 of the blank value carried by the persulfate oxidizer. To obtain the final sample TDN concentration in  $\mu$ M, multiply the result by 3.

#### **Interferences**

Sample turbidity, concentrations of iron, copper or other metals above several mg/L, oil and grease and residual chlorine can interfere with this analysis. Sample turbidity can be eliminated

by filtration and by settling. Metal interferences can be removed by the addition of EDTA into the buffer. Oil and grease can be removed by distillation.

## **Quality Assurance/Quality Control**

### **Blanks:**

3 oxidizer and 2 MilliQ blanks are digested with each sample set.

Standard additions are run on 10% of samples and must have recovery of 80-120% to pass.

### **Standard Additions:**

$$\% \text{ Recovery} = ((x(a) - x(0)) / \text{std add}) * 100$$

$x(a)$  = concentration of sample with spike

$x(0)$  = concentration of sample without spike

std add = concentration of the spike added

## **Method Detection Limit**

The method detection limit for this assay is 0.1  $\mu\text{M}$ .

## **References**

Standard Methods for the Examination of Water and Wastewater. 19<sup>th</sup> edition. Method 4500-Norg.

D'Elia, C.F., P.A. Stuedler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22: 760-764.

## **Coastal Systems Analytical Facility**

### **Laboratory SOP: Nitrate+Nitrite**

Revised: 15-Nov-02 (DSW & BLH)

#### **Introduction:**

Nitrate+nitrite ( $\text{NO}_3+\text{NO}_2$ ) are present in surface water, ground water and the sediment pore water of both fresh water and marine ecosystems. Samples are pre-filtered through a  $0.45\text{ }\mu\text{m}$  membrane filter. Analysis is by an auto-analyzer (Lachat) using copperized cadmium reduction and colorimetric assay.

#### **Equipment:**

Lachat QuikChem 8000 with filter for 520nm wavelength  
1 liter volumetric flasks  
2 liter wide mouth plastic bottle  
Adjustable Eppendorf Pipette

#### **Consumable Supplies:**

Potassium Nitrate  $\text{KNO}_3$  (Fisher Number P263-500)  
Sodium Nitrite  $\text{NaNO}_2$  (Fisher Number S347-500)  
Sodium Chloride  $\text{NaCl}$  (Fisher Number S271-3)  
Magnesium Sulfate  $\text{MgSO}_4\bullet7\text{H}_2\text{O}$  (Fisher Number M63-500)  
Sodium Bicarbonate  $\text{NaHCO}_3$  (Fisher Number S233-500)  
Ammonium Chloride  $\text{NH}_4\text{Cl}$  (Fisher Number A661-500)  
Sodium Hydroxide  $\text{NaOH}$  (Fisher Number S318-1)  
Phosphoric Acid  $\text{H}_3\text{PO}_4$  (Fisher Number A242-212)  
N-(1-naphthyl)-ethylenediamine dihydrochloride (NED) (Fisher Number LC17550-1)  
Sulfanilimide 4- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$  (Fisher Number O4525-100)  
Hydrochloric Acid  $\text{HCl}$  (Fisher Number A144C-212)  
Copper Sulfate  $\text{CuSO}_4\bullet5\text{H}_2\text{O}$  (Fisher Number C493-500)  
15X85mm borosilicate test tubes for standards  
12X75mm borosilicate test tubes for samples

#### **Preparation of Samples**

Pour off sample into 13 X 100 mm borosilicate test tube. Place in auto sampler tray. Type in sample IDs on the Omnitron program.

#### **Calculations**

Concentrations are determined by the software associated with the system automatically. The standard regression equation for the lower and upper parts of the curve is determined. The absorbances of the samples are sorted such that the lower absorbances are converted to concentration using the regression equation for the lower standards. Samples with absorbances in the higher range are converted to concentrations using the higher regression equation.

Equation: concentration ( $\mu\text{M}$ ) = 
$$\frac{(\text{absorbance} - \text{intercept})}{\text{slope}}$$

## **Data reduction**

### **Peak optimization:**

The integration window of the peak is determined to be a 3 second window on either side of the high-heat point of the peak.

## **Quality Assurance/Quality Control**

### **Internally programmed system QA/QC:**

Standard curve must have an r value of .9950 or greater.

Residuals greater than 10% are flagged.

Check standards are run every 12 samples and must be within 10% of expected values.

A column check using a known NO<sub>2</sub> standard is run at the beginning of the tray and must give an efficiency greater than 88%.

Lab duplicates are run on 10% of the samples and must be within 10% of each other for the system to be in control.

Blanks are run twice per sample set.

Standard additions are run every ninth sample and must have recovery of 80-120% to pass.

Method	0-10uM Method	0-50uM Method	0-700uM Method
Sample volume (ml)	5ml	5ml	5ml
Spike: ml of 5,000uM stock NO <sub>3</sub> to add	2.5ul Gives 5uM spike	10ul Gives 10uM spike	100ul Gives 100uM spike

If standard addition is not between acceptable recovery limits then the analysis is out of control and the problem must be determined and std. addition repeated until there is 80-120% recovery. Standard additions are added to a sample such that the volume change is negligible and the spike will fall in the middle of the standard curve range.

### **Standard Additions:**

% Recovery =  $((x(a) - x(0))/\text{std add}) * 100$

x(a) = concentration of sample with spike

x(0) = concentration of sample without spike

std add = concentration of the spike added

Dilutions: If a sample is greater than the highest standard it is auto diluted with the matrix.

## **Method Detection Limit**

The Method Detection Limit (MDL) is 0.1uM.

## **Interferences**

Sample turbidity, concentrations of iron, copper or other metals above several mg/L, oil and grease and residual chlorine can interfere with this analysis. Sample turbidity can be eliminated by filtration and by settling. Metal interferences can be removed by the addition of EDTA into the buffer. Oil and grease can be removed by distillation.

### **References**

Standard Methods for the Examination of Water and Wastewater, 19<sup>th</sup> edition. Method 4500-NO3-F.

Lachat Autoanalysis procedures based upon the following techniques:

Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. *J. Mar. Biol. Ass. U.K.* 47:23-31.

Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in seawater. *J. Mar. Res.* 11:87-96.

# Total Phosphorus/Total Dissolved Phosphorus by Acid Persulfate Digestion

---

Revised 2008

## Introduction

Organically bound phosphorus is converted to orthophosphate by oxidation destruction of both dissolved and suspended organic phosphorus with persulfate under acidic conditions.

## Equipment

1 liter Volumetric Flasks

Transfer Pipettes, 10-25 ml

Eppendorf Pipettes, 10-100  $\mu$ L, 100-1000  $\mu$ L

## Consumable Supplies

Potassium persulfate  $K_2S_2O_8$  (Fisher Number P282-500)

Sulfuric Acid  $H_2SO_4$  (Fisher Number A300-212)

$Na_2HPO_4$ , Dibasic  $Na_2HPO_4$  (Fisher Number S374-500)

Ammonium Molybdate  $(NH_4)_6Mo_7O_{24} \bullet 4H_2O$  (Fisher Number A674-500)

Autoclavable 25 x 125 mm screw cap test tubes

Autoclavable screw caps

15 X 85 mm borosilicate test tubes

## Preparation of Samples

1. For total P, samples are unfiltered; for Total Dissolved P, samples are pre-filtered with a 0.22  $\mu$  filter.
2. In a labeled 16x125 mm test tube add 10 ml sample.

## Adding Reagent

1. Add 3.2 ml of the potassium persulfate reagent to each test tube (samples and standards).
2. Then add 0.05 ml 5.6M sulfuric acid to each tube.
3. Cap with an autoclavable test tube cap.
4. Autoclave at 121° C for 30 minutes.

## Data Calculations

Final concentrations are determined by multiplying the concentrations obtained with the Ortho-Phosphate assay by the appropriate dilution factor.

### **Quality Assurance/Quality Control**

1. Blanks will be run on a minimum of 5% of the sample load and after any samples that are off scale.
2. Field duplicates are collected for 5% of the sample set.
3. Five lab duplicates should be analyzed for each run.
4. Standard Additions will be run on at least 5 samples each day for each set of samples analyzed. Standard Additions must be between 80 and 120% recovery to pass. If standard addition is not between acceptable recovery limits then the problem must be determined and std. addition repeated until there is 80-120% recovery. Standard additions will be added to a sample such that the volume change will be negligible and the spike will fall in the middle of the standard curve range.

Standard Additions:

Add 50 uL of a 1 mM PO<sub>4</sub> standard to a sample

% Recovery =  $((x(a) - x(0))/\text{std add}) * 100$

x(a) = concentration of sample with spike

x(0) = concentration of sample without spike

std add = concentration of the spike added

### **Method Detection Limit**

The Method Detection Limit (MDL) is 0.05  $\mu\text{M}$ .

### **Notes:**

1. Due to dilution effects from adding persulfate to each sample, the sensitivity of this method is less than that of the method using boiling nitric and sulfuric acids. This method works best with samples that are significantly higher in concentration than the method detection limit of 0.05  $\mu\text{M}$ .
2. The final assay is our standard Murphy and Riley ortho-phosphate method run on the digest. For this assay, the molybdate reagent used is made with 24 g of ammonium molybdate per 500 mls instead of 20 g. The persulfate digestions are acidic and increasing the molybdate concentration makes the assay more sensitive when used with samples that are acidic.
3. In addition to samples, MilliQ blanks and a complete standard curve need to be put through the entire digestion.

### **References**

Standard Methods for the Examination of Water and Wastewater, 17<sup>th</sup> edition, 1989, p. 4-172.  
Modification of a technique for Total Dissolved Nitrogen from: D'Elia, C.F., P.A. Stuedler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22: 760-764.

## **Coastal Systems Analytical Laboratory**

### **Laboratory SOP: Chlorophyll a & Pheophytin a**

---

Revised: 15-Nov-02 (DSW & BLH)

#### **Introduction:**

Chlorophyll is a light sensitive pigment, which degrades in the presence of light and warm temperatures. Filtering and assay should be performed in a dimly lit room. Samples should have been collected in 1 liter dark polyethylene bottles and transported on ice. They should be filtered upon arrival at the laboratory. Sample filters should be either extracted immediately or stored in foil in the freezer for later assay.

#### **Equipment:**

Vacuum filtering apparatus and filtering towers for 47 mm 0.22  $\mu$  membrane filters  
Turner Designs 10-AU Fluorometer  
1 pair filter forceps  
250 ml graduated cylinder (6)  
250 ml wash bottle

#### **Consumable Supplies:**

47 mm Nucleopore membrane filters  
1 dram vials  
Kimwipe tissues  
Pasteur Pipettes  
Magnesium Carbonate MgCO<sub>3</sub> (Fisher Number M27-500)  
Acetone (Fisher Number A18-4)  
Distilled/Deionized water  
Turner Certified Chlorophyll Standards  
16 X 125 mm borosilicate test tubes

## Procedure

### Preparation of Samples: Filtration

1. All filtering must be done in the dark with a green light, or, if not possible, in a dimly lit room with no direct lighting of any kind
2. Pre-label dram vials for each sample
3. Using filter forceps, place a 47 mm Millipore filter on a filter holder on one of the filtering towers. Attach tower.
4. Shake sample bottle and rinse graduate cylinder with ~100 ml of sample.
5. Again, shake sample bottle and measure 200 ml of sample into graduate cylinder.
6. Turn on vacuum pump. Pour out 50-100 ml increments into filter funnel. Once sample has been added, it cannot be withdrawn. Be sure to keep an accurate track of the cumulative volume of water filtered. **Do not let the filter go dry.**
7. After sufficient sample has been added (filtering rate should be very slow, indicating filter is clogged with particulate matter) and **before the last of the added sample has passed through the Nucleopore filter**, add 3 drops of the  $MgCO_3$  solution with a Pasteur pipette around the surface of the filter. Then Rinse funnel with a squirt of distilled water from the wash bottle.
8. Allow the remainder of the sample to filter through till the filter is dry.
9. Fold the filter in half without touching the filtered material. Then fold again along the same axis as the first fold. Place into a pre-labeled dram vial.
10. Add 10 ml of 90% acetone to the test tube and cap.
11. Shake the test tube until the filter is in the middle of the test tube and it has opened up, exposing the sample to the acetone. Grind with glass pestle. Cap tube.
12. Place the test tube in the test tube rack and label its location on the analysis form.

### Sample Analysis

The following should be performed in the lab under dim light or preferably in the dark with a green light.

1. When samples are ready to read, turn the Fluorometer on, let warm up 10 min.
2. Take the samples out of the freezer. Unwrap the rack and shake each test tube, keeping your finger on top of the cap while shaking.
3. Wrap the rack back up and return to freezer for 0.5-1.0 hour.
4. Calibrate the Fluorometer according to the procedure outlined above.
5. If there is any floc in the sample test tube, make sure that it has settled, transfer the sample to a cuvette.
6. Wipe the outside of each cuvette with a clean kimwipe before reading the sample on the Fluorometer.
7. Insert the sample cuvette, wait for the readout to stabilize and record
8. Once the chlorophyll a concentration is read and the data recorded, add **1 drop** of 10% HCl to the cuvette, swirl, and insert the cuvette, wait 90 seconds and re-read the sample for phaeo pigments. Record the result.
9. Add another drop of 10% HCl to the cuvette, re-insert, read and record data again.
10. Repeat 13-17 for all samples.
11. When finished rinse out all cuvettes and turn off the Fluorometer.

### Interferences

Turbidity from dissolved 0.22  $\mu$  membrane filters can cause interference with the fluorometer. The sample is allowed to settle in the extraction tube before it is pipetted into the cuvette.

### **Quality Assurance/Quality Control**

1. Blanks are run on a minimum of 5% of the sample load and after any samples that are off scale.
2. Field duplicates are collected for 5% of the sample set.
3. A minimum of 5 check standards (certified) are run as samples each day for each set of samples analyzed. Check standard must be between 80 and 120% of the known standard concentration. If the check standard is not between acceptable recovery limits then the problem must be determined, corrected and the check standard re-run so that it falls between 80-120% of the standard concentration value.
4. Dilutions: If a sample is greater than 10% of the highest standard it must be diluted with MilliQ.

### **Method Detection Limit**

The Method Detection Limit (MDL) is 0.1  $\mu$ g/cm<sup>3</sup>.

### **References**

Standard Methods for the Examination of Water and Wastewater, 17<sup>th</sup> edition, 1989, p. 10-31.

Parsons, T.R., Y. Maita and C. Lalli. 1989. Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, 173 pp.

---

# Coastal Systems Analytical Facility

## Laboratory SOP: pH and Alkalinity

---

### **Introduction:**

Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases. Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents.

### **Equipment**

Titroline 96  
100mL graduated cylinder

### **Consumable Supplies**

Buffer Soltion pH 7.0 (Fisher Number SB107-500)  
Buffer Solution pH 4.0 (Fisher NumberSB101-500)  
Hydrochloric Acid Solution N/50 (Fisher NumberSA60-1)  
3M KCl (Fisher Number BP366-1)  
150mL plastic beakers  
Stir Bar

### **Preparation of Samples**

Calibrate Titroline 96 using 4pH and 7pH standards.

Set end point to a pH of 4.7

Pour off 100mL sample and place under probes

Press start and record the initial pH value

Titrate 100mL sample using 0.02N standard acid solution (0.02N HCl)

The Titroline 96 will titrate the sample down to a pH end point of 4.7. Record the mL titrated

Set the end point to 4.4 and run the same sample until the end point is reached. Record the mL titrated. Record the volume titrated (mL)

### **Calculation:**

Alkalinity (mg CaCO<sub>3</sub>/L)

$$=(2B -C) \times 50000 \times N / 1000$$

B= mL titrant to first recorded pH

C= total mL titrant to reach pH 0.3 unit lower

N= normality of acid

### **Quality Assurance/Quality Control**

Field duplicates are collected for 5% of the sample set.

lab duplicates should be run each day

Check standards should be run each day

### **Method Detection Limit**

The Method Detection Limit (MDL) is 0.05mg CaCO<sub>3</sub>/L

### **Reference:**

Standard Methods for the Examination of Water and Wastewater, Method 2320-B, 19<sup>th</sup> edition, 1995.

# Coastal Systems Analytical Facility

## Laboratory SOP: Dissolved Oxygen

---

Revised: 15-Nov-02 (DSW & BLH)

### **Introduction:**

Dissolved oxygen is an important parameter for biological systems and therefore is used in the assessment of water quality in natural systems. It is measured by the wet chemical Winkler Method with assay by potentiometric auto-titrator.

### **Equipment:**

Radiometer ABU Autoburette Titrator  
100 ml volumetric pipet and bulb  
1 liter reagent bottle  
magnetic stir bars  
300 ml BOD bottles  
overflow container

### **Consumable Supplies:**

150 ml polystyrene sample cups

Winkler Reagents:

Manganous sulfate  $MnSO_4 \cdot H_2O$  (HACH No. 1071-66)  
Alkaline Iodide Azide (HACH No. 1072-66)  
Sulfamic Acid  $H_2NSO_3H$  (HACH No. 1073-99)

Saturated Potassium Chloride KCl (Fisher No. P217-500)

Standardized Sodium Thiosulfate Solution  $Na_2S_2O_3$  (0.0248 – 0.0252 N) (Fisher No. SS370-1)

### **Adding Reagents and Reading Results**

1. Check reference electrode on the Autoburette Titrator to see that KCl crystals are free-flowing and without any trapped air bubbles. Remove bottom cap. Remove plastic hole-plug from side of electrode, add more KCl if needed so the solution is within ¼ inch of the filling hole, slide rubber sleeve up so the top of the sleeve is just above the filling hole. Rinse electrode with DI and return to electrode holder. Bottoms of the electrodes should be vertically aligned within ½ inch of each other.
2. Turn on titrator by depressing switch on left rear side.
3. Put a beaker below the electrodes. Press FLUSH to flush titrant through red tubing. If any air bubbles are in the tubing, tap it to dislodge the bubbles. If all the bubbles do not flush through, repeat the FLUSH cycle. Rinse electrodes with DI. Discard titrant from the flush cycle and rinse out beaker.
4. Rinse electrodes with DI, lower electrodes into sample which in turn starts the stirrer. On the first titration of the day, use the UP ARROW to adjust the stirring speed to 2.
5. Press RUN. Record start mV number from the top of the display.
6. At the end of the titration, the light next to REMOTE will go off. Press RESULT, record ml and end mV. Press DOWN ARROW, record ml and value (move display decimal point 2 places to the right to get  $\mu M O_2$  (i.e. 2.782 on the display = 278.2  $\mu M O_2$ ).
7. Rinse electrodes with DI, then proceed as above with remaining samples.

8. Don't let the reference electrode dry out. If it must be left unattended for a period of time, lower the electrodes into a beaker of DI.
9. After running the last sample, rinse electrodes, slide down the sleeve of the reference electrode, replace the filler hole plug, put DI in the cap and slide over bottom of the electrode. Return to electrode holder.
10. Turn off the titrator by depressing the button on the back left side. Cover the screen with the black plastic rectangle.
11. Turn off autopipettor. Rinse pipet inside and out with tap water followed by DI.

### **Quality Assurance/Quality Control**

1. Field duplicates are collected for 5% of the sample set.
2. Check standards are run after every 10 samples. Check standard must be between 80 and 120% of the known standard concentration. If the check standard is not between acceptable recovery limits then the problem must be determined, corrected and the check standard re-run so that it falls between 80-120% of the standard concentration value.

### **Method Detection Limit**

The method detection limit for this procedure is 0.1  $\mu\text{M}$

### **References**

Standard Methods for the Examination of Water and Wastewater, 17<sup>th</sup> edition, 1989. Pp. 4-149.

TitraLab<sup>TM</sup> Users Handbook, Radiometer Analytical A/S, Bagsvaerd, Denmark.

# Coastal Systems Analytical Facility

## Laboratory SOP: Temperature

---

Revised: 15-Nov-02 (DSW & BLH)

### **Introduction:**

Temperature is measured in aquatic ecosystems for a variety of reasons. Temperature data are used to calculate saturation of dissolved oxygen, salinity and density. Temperature data are used to determine depth-specific properties of water in lakes, ponds and embayments, such as the position and condition of the thermocline and pycnocline.

### **Equipment:**

Standard Celsius mercury-filled field thermometer with a range of -5°C to +40°C, a precision of  $\pm 0.5^{\circ}\text{C}$  and an accuracy of 1°C.

Standard thermister with a range of -5°C to +40°C, a precision of  $\pm 0.1^{\circ}\text{C}$  and an accuracy of 0.2°C.

NIST-Certified precision calibration thermometer with a range of -1°C to +101°C, a precision of  $\pm 0.04^{\circ}\text{C}$  and an accuracy of 0.1°C.

### **Calibration**

#### ***Field Thermometer***

The field thermometer and the calibration thermometer are placed in a series of beakers of water at different temperatures. The temperature readings of both thermometers are recorded over at least 5 different temperatures within the range of field temperatures expected. The field thermometer data are then regressed against the calibration thermometer data. The coefficient of determination ( $r^2$ ) for the regression should be at least 0.99 and no pair of temperature points should have a difference of more than 1.0°C.

#### ***Thermister***

The thermister is factory calibrated. Before use in the field, the thermister is placed in a beaker of ice water with the calibration thermometer. The temperature of each is recorded. The difference between the thermister reading and the reading of the calibration thermometer is calculated and used to correct the data after field work has been completed.

### **Procedure**

1. The field thermometer or thermister is placed in the container of water being measured or in the water column in the field.
2. The thermometer/thermister is allowed to equilibrate with the water until a stable temperature reading is recorded.
3. The thermometer/thermister is then placed in the next container to be measured or moved to the next depth in the water column and the process is repeated.
4. When all readings are completed, the thermometer or thermister is rinsed, dried and returned to its case.

### **References**

Standard Methods for the Examination of Water and Wastewater, Method 2500, 19<sup>th</sup> edition, method 1995.