Plymouth Ponds and Lakes Stewardship (PALS) Project

Monitoring Program and Pond Management Plans

A Partnership of
Town of Plymouth
Department of Marine & Environmental Affairs

with
Coastal Systems Program
School for Marine Science and Technology
University of Massachusetts Dartmouth

Quality Assurance Project Plan 2020-2022

Prepared by:
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May 2020

Approval Page
Town of Plymouth, Department of Marine & Environmental Affairs and
Coastal Systems Program, SMAST/UMassD and
MassDEP QAPP Review

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1. Distribution List

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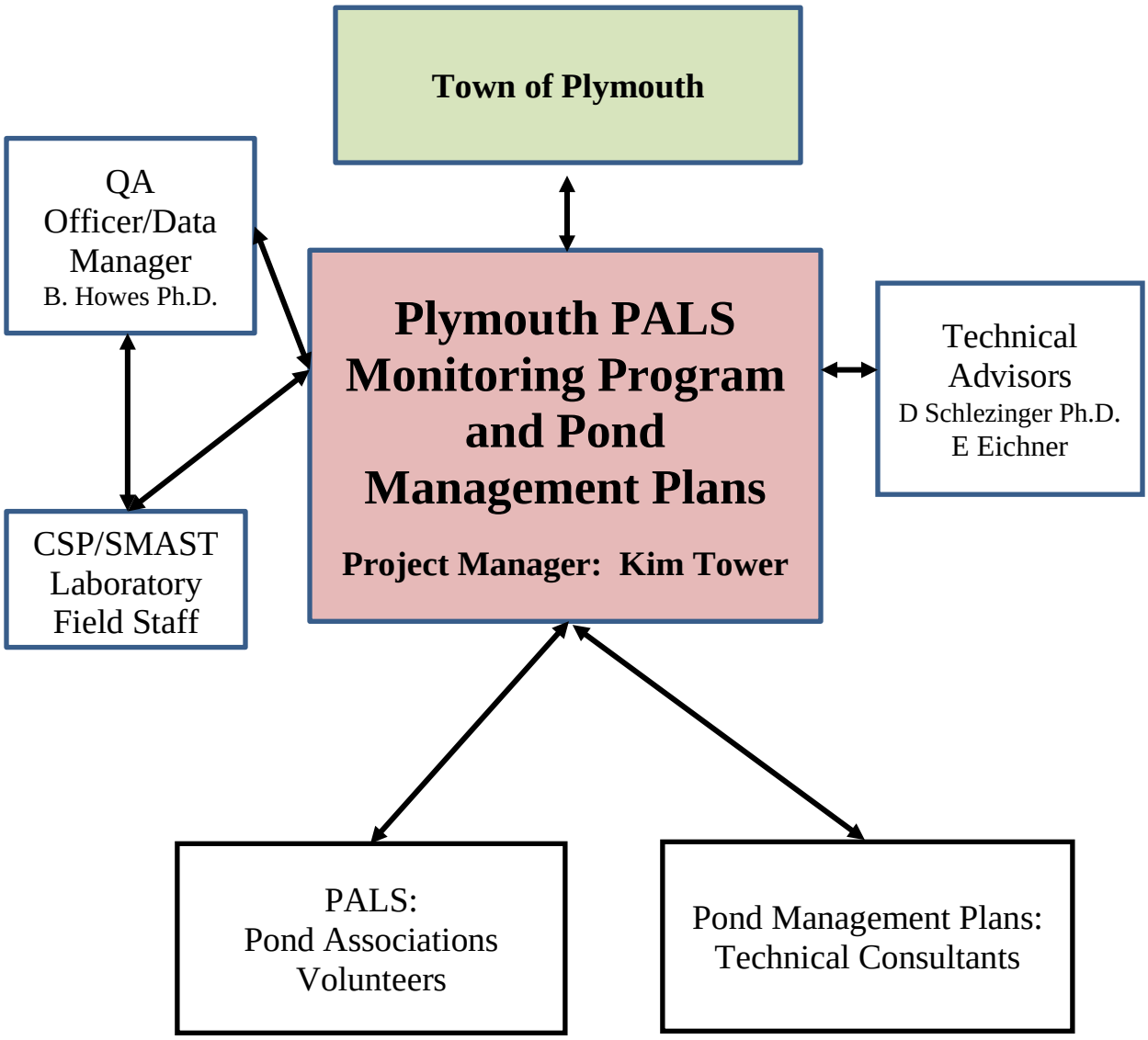
2. Program Organizational Chart



2.1 Project Partners and Responsibilities

Title	Responsibilities
Project Manager	Manage project finances, coordinate PALS sampling with pond associations, coordinate sampling and training of PALS volunteers with CSP/SMAST, coordinate and review development of pond management plans, including sampling, development, public discussion and acceptance, regulatory approval, and implementation Project Manager: Kim Tower
Technical Advisors	Assist with development of PALS and selected pond management plan program objectives, attain data quality objectives, and ensure appropriate methods, including laboratory assays, field data collection, and data analysis. Facilitate assistance in the development and implementation of PALS sampling and pond management plans, implementation of associated action plans and management plans when possible. David Schlezinger and Eduard Eichner
Field Staff/Volunteers	PALS sampling volunteers will be trained with sampling procedures and will conduct sampling of multiple ponds. During the PALS snapshot, ponds not sampled by volunteers will be divided among town and CSP/SMAST field staff. Town and CSP/SMAST field staff will coordinate to ensure that sampling procedures are the same. CSP/SMAST field staff will be responsible delivery of samples to the laboratory according to QAPP procedures.
Laboratory	Coastal Systems Analytical Facility Laboratory, School of Marine Science and Technology (SMAST) provides analysis of water samples specifically for nutrients and nutrient-related constituents at the low concentrations typically found in surface waters. Lab will provide appropriate sample containers and coolers for sample collection and transport during both PALS snapshot and any sampling associated with pond management plans. Samples handling and assays will be conducted using standard methods. The lab performs all quality control checks as required by their QAPP. All assay results will be provided in a timely fashion and, if completed for a management plan, will be reviewed and summarized in the plan. Lab staff will work with Project Manager and Technical Advisors, and others as appropriate, to resolve any issues that may arise. Brian Howes, Director; Sara Sampieri, Facility Manager
Data Manager	Data from the Lab and field data are collated by Data Manager. Data is maintained by Data Manager and shared with Project Manager. Project Manager will make the data public via the town website. Project Manager: Kim Tower; Data Manager: Eduard Eichner
QA Project Officer	Brian Howes, Ph.D, Chancellor Professor at the School of Marine Science and Technology is identified as the Quality Assurance Project Officer whom independently reviews seasons data and Quality Control results for compliance.

3. Plymouth PALS Introduction

The Town of Plymouth Department of Marine & Environmental Affairs (DMEA) mission, in part, is to provide for the protection, preservation, enhancement and safe use of the Town's natural resources and to address environmental issues that threaten or may negatively impact the health, welfare, and quality of life of the Town's citizens. In the late 1970's the Town conducted baseline water quality surveys for 41 ponds, but have been limited to periodic snapshots of individual ponds since then. The Town of Plymouth frequently receives inquiries from the residents regarding the water quality of their ponds and whether any data has been collected. The Town DMEA and the Conservation Commission continually refer to the 1970's reports, over forty years old, to answer many of these questions. Many of the concerns are in regard to eutrophication of various water bodies. The Town received Massachusetts Environmental Trust (MET) funding in 2014 to initiate an effort called the Plymouth Pond and Lakes Stewards (PALS) program to begin to collect new data from the town's ponds, organize and evaluate old and new data, and provide feedback to citizens and town decision-makers about pond status and management concerns. This has been a successful program to date and the continuation of the program will provide valuable data to the Town, Watershed Association and the State in evaluating water quality. Since the PALS program was initiated, the Town, volunteers, and pond associations have become increasing interested in developing pond management plans that include the PALS data and more refined targeted data necessary to develop reliable plans.

The Plymouth PALS snapshot is a monitoring program that is designed to provide initial and long-term data about the status of selected ponds. The 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 16 years. Water quality results from the first Plymouth PALS snapshot were reviewed in the 2015 Plymouth Pond and Lake Atlas.[1] The Atlas included development of a listing of all ponds, organization and synthesis of past sampling data, comparison of current data to past data, and feedback to pond associations and other decision-makers on the status of individual ponds. PALS snapshots have occurred annually since completion of the first snapshot.

The startup of the Plymouth PALS program created an interest among many of the homeowner and lake associations to develop pond management plans to address some of the water quality problems identified through the PALS snapshots. These management plans were anticipated as more refined, focused studies that included targeted data collection for key parameters that are not addressed through the water column snapshots, including bathymetry, streamflows and associated nutrient loads, phytoplankton and rooted plant surveys, and sediment nutrient regeneration measurements. The Town is including minimum protocols for these measures to ensure that management plans will address any anticipated TMDL concerns as the Town moves forward with comprehensive water quality management.

One of the primary goals of the Plymouth PALS program is to engage and educate the community. This project will include involvement of several watershed associations as well as smaller

[1] Eichner, E.M., B.L. Howes, and S. Horvet. 2015. Town of Plymouth Pond and Lake Atlas. Town of Plymouth, Massachusetts. Coastal Systems Program, School for Marine Science and Technology, University of Massachusetts Dartmouth. New Bedford, MA. 138 pp.

homeowner associations and areas where associations have not been developed. In addition, the Town will actively engage with individual homeowners and groups of homeowners to address any concerns that arise during the development of pond management plans.

4. Plymouth PALS Project Partners

The project partners share many of the same goals and philosophies including adequate information to develop water quality management strategies and ensure the protection of the ponds and their associated ecosystems. The Town is committed to ensuring that pond ecosystems are managed appropriately through an integrated partnership with pond and lake associations, homeowner associations, and other volunteer monitoring partners. The key to appropriate management is reliable data and regular feedback. Coastal Systems Program at the School for Marine Science and Technology, University of Massachusetts Dartmouth (CSP/SMAST) can help the town and associations meet their goals by sharing expertise and guidance in order to provide high quality scientific support for effective management of these resources.

4.1 Town of Plymouth

The Town of Plymouth is municipality consisting of approximately 55,000 residents of various age, gender and income levels. Plymouth has the largest area (65,775 acres) among the 351 cities and towns in Massachusetts and has over 70 freshwater ponds of greater than 10 acres ("Great Ponds" under MGL, Chapter 91) and a total of over 200 ponds. The Town is distributed by five villages: North Plymouth, West Plymouth, Plymouth Center, Manomet and Cedarville.

The Town of Plymouth Department of Marine & Environmental Affairs (DMEA) mission is to provide services that protect the safety of people and vessels who use our waterways and waterside facilities; including rivers, ponds and lakes; to provide for the protection, preservation, enhancement and safe use of the Town's natural resources, including beaches, conservation lands and preserved open spaces; and to address environmental issues that threaten or may negatively impact the health, welfare, and quality of life of our citizens. DMEA is involved in a variety of projects including stormwater remediation, water quality sampling and reporting, dam removal and river restoration, wetland restoration and land acquisition.

The Plymouth PALS program addresses the Town of Plymouth need to restore and maintain the chemical, physical and biological integrity of our waterbodies as specified in the Clean Water Act and town regulations. In the late 1970's the Town conducted baseline water quality surveys for 41 ponds in Plymouth, but have been limited to periodic snapshots of individual ponds since then. Watersheds Associations have assisted by collecting limited data with their available resources.

The Town DMEA completed the initial 2014 PALS snapshot to begin to regularly develop additional, updated water quality data for the town's ponds and lakes. Since the initial snapshot, the Town has conducted annual snapshots and this, in turn, has created Town interest in developing pond management plans that will address TMDL issues and comprehensive water quality management of surface water throughout the town. DMEA has recently begun to efforts to prioritize the completion of pond management plans.

Several ponds and lakes in Plymouth are listed as impaired in the MassDEP Integrated List, but the majority has not been adequately characterized. Many of the ponds also include resource areas listed in the Natural Heritage Priority & Estimated Habitats and are important resources for

recreational and homeowner uses. These types of coastal plain ponds are relatively unique and the majority of their global distribution is within Plymouth & Barnstable Counties.

4.2 Coastal Systems Program, School for Marine Science and Technology, University of Massachusetts Dartmouth

The Coastal Systems Program at the School for Marine Science and Technology, University of Massachusetts Dartmouth (CSP/SMAST) provides a full range of lake and pond assessment, monitoring, and management skills with extensive experience in developing assessments of point and non-point source impacts, watersheds, water quality, and ecosystems, as well as associated development of options and strategies to attain management goals. Our experts are well recognized for developing diversified approaches to meet client goals and provide sound environmental solutions. CSP/SMAST maintains staff scientists and support personnel that are supplemented on a project basis by specialists throughout the U.S.

CSP/SMAST was established to provide research quality information to address the growing ecological degradation of coastal ecosystems and, through expanded demand, has more recently begun to apply many of the same tools to freshwater systems. Staff fills the niche between basic and applied research by providing high quality scientific support for management of surface waters (bays, harbors, wetlands, ponds/lakes, and watersheds). We evaluate nutrient-related water quality issues, providing information fundamental to developing data driven management plans for the protection of surface waters. These efforts have generally integrated investigation of nutrient inputs with transformations and losses from their sources to understand their ultimate fate and impact on the ecological health of water ecosystems. Communities throughout Southeastern Massachusetts currently use data generated by the CSP/SMAST laboratory and analysis and water quality recommendations prepared by CSP/SMAST staff for management and policy decisions regarding restoration, remediation, and protection of coastal and freshwater systems.

CSP/SMAST is a leader in freshwater pond monitoring and assessment. CSP/SMAST has partnered with towns, cities, regional government, advocacy groups, trade associations, pond associations and state agencies throughout southeastern Massachusetts. CSP/SMAST is a partner with the Cape Cod Commission and the towns of Barnstable County to provide laboratory services for 19 years of the Cape Cod Pond and Lake Stewards (PALS) Snapshots. These Snapshots are citizen-based water quality sampling of ponds throughout Cape Cod during the late summer and have regularly included 150 or more ponds. This data has been invaluable in creating a region-wide pond monitoring culture that has expanded throughout southeastern Massachusetts and has empowered groups of citizen stewards. This, in turn, has led to more intensive pond-specific assessments and development of management strategies.

CSP/SMAST staff has also completed diagnostic pond assessments and management plans for more than 30 ponds and lakes in the past 10 years. Recent assessments have included:

a) intensive, citizen-based, pond water quality sampling programs,
b) sediment core collection and incubation to nutrient regeneration rates
c) watershed delineations, land use assessments and estimates of nutrient loads
d) monitoring and characterization of cranberry bogs and interactions with ponds,
e) aquatic bird, mussel, and plant surveys,
f) monitoring of incoming and outflowing streamflow and associated nutrient loads, and
g) stormwater monitoring, including individual storm monitoring, discharge point watersheds

Our ability to work with organizational staff, town and regional boards, and consulting firms while coordinating activities with state agencies has led to effective pond and lake assessments and management strategies. Recent projects have included a water quality assessment and subsequent management plans for: Scargo Lake in Dennis; Lower Mill Pond, Upper Mill Pond, and Walkers Pond in Brewster; Uncle Harveys Pond and Pilgrim Lake in Orleans, and a water quality assessment and TMDL strategies for White Island Pond in Plymouth/Wareham. Past pond and lake project partners have included the Towns of Barnstable, Brewster, Orleans, Eastham, Harwich, Westport, the Cape Cod Cranberry Growers Association, MassDEP, the Lake Wequaquet Protective Association, and the Indian Ponds Association.

CSP/SMAST will provide logistical, educational and data synthesis center for water quality monitoring throughout both the PALS Snapshots and any pond management plans for which CSP/SMAST is selected. CSP/SMAST is fully equipped for the field and analytical requirements of water quality research including: automated nutrient analyzers (LACHAT), field (SeaTech) fluorometers, ion (Dionex) & gas (ECD, TCD, FID) chromatographs, mass spectrometers (Finnegan), CTD's (Seabird), LECO Total Sulfur Analyzer, water and sediment sampling gear, field automated samplers (ISCO), Marsh-McBurney electromagnetic flow meters, field moorings for oxygen, temperature, salinity, depth (Endeco & WHOI), and a coastal vessel. Specific to nutrient related research are the automated nutrient analyzers, Turner AU10 laboratory fluorometer, Radiometer SB10 potentiometric oxygen titrator, Buchler chloridometer, Eh and pH electrodes and meters, scanning spectrophotometers (Spectronic 2000 & Spectronic 801), CO2 Infrared analyzers, Perkin Elmer PE2400 automated CHN analyzer, plus the full suite of analytical balances, drying ovens, autoclaves, walk-in freezers & refrigerators, radiochemistry laboratory, glove boxes, and Niskin and pump samplers. CSP/SMAST currently runs over 30,000 chemical assays of water samples each year for federal, state, and numerous municipal and research groups, including: US Environmental Protection Agency, US Army Corps of Engineers, US Department of Energy, US Department of Defense, MassDEP, Rhode Island Department of Environmental Management, and South Florida Water Management District.

4.3 Pond Associations and other sampling partners

Pond Associations with long-standing monitoring programs will provide volunteers for PALS Snapshots and outreach for pond management plans. Volunteer samplers from other ponds will also be recruited through contacts developed during public discussion of the PALS program and outreach to other organizations, such as homeowner associations. All participating sampling volunteers will be trained to follow PALS Snapshot sampling protocols.

Pond management plans will be developed in coordination among the Town and a selected consultant. Regular interaction with pond associations, homeowner associations, and similar pond stakeholder groups will be part of pond management plan development and approval.

LIST OF CONFIRMED POND ASSOCIATION AND OTHER MONITORING PROJECT PARTNERS			
Partner	**Contact Info**	**Roles and Responsibilities**	**Pond/River Monitoring Experience (years)**
Herring Ponds Association	www.theherringpondswatershed.org Don Williams donald_r_williams2003@yahoo.com	Collect water samples; Public outreach	8
Billington Sea Association	www.billingtonseapond.com Mike Leary mleary_154@comcast.net	Collect water samples; Public outreach	13+
Six Ponds Association	www.sixponds.org Ed Russell edrussel@aol.com	Collect water samples; Public outreach	33+
Friends of Ellisville Marsh	http://ellisvillemarsh.org/ Eric Cody eric@ellisvillemarsh.org	Collect water samples; Public outreach	18+
Savery Pond Conservancy	www.saverypond.org Peter Schwartzman peter@saverypond.org	Collect water samples; Public outreach	6+

5. Ponds to be regularly targeted for sampling during PALS Snapshots

During the initial 2014 PALS Snapshot, sufficient volunteers have been recruited to sample most ponds; and with staff from the Town and/or 40 ponds were sampled. The Town has initially focused on Great Ponds in Plymouth as well as ponds that the Town has received public interest in knowing about water quality. In some areas, ponds will be sampled regularly depending on staff time, volunteer and funding availability. This list will be adjusted annually by Plymouth DMEA in consultation with CSP/SMAST.

Pond	Acerage	Max Depth	Sampler
Great Herring Pond	419	14.02	Town/HPWA
Little Herring Pond	81	1.83	Town/HPWA
Honeypot Lake	19	NA	Town
Boot Pond	74	10.97	Town
Savery Pond	30	3.66	Town/FOEM
Rocky Pond	22	5.79	Town
Little Rocky Pond	12	NA	Town
Long Duck Pond	28	NA	Town
Little Long Pond	50	2.44	SPWA
Long Pond	224	31.09	SPWA
Halfway Pond	229	3.96	SPWA
Round Pond	22	7.3	SPWA
Gallows Pond	51	10	SPWA
Bloody Pond	98	11.58	SPWA
Eel River Pond	21	NA	Town
Charge Pond	18	7.31	Town
College Pond	50	7.31	Town
Curlew Pond	45	NA	Town
Fearing Pond	27	6.09	Town
Abner Pond	11	NA	Town
Bumps Pond	19	NA	Town
Three Cornered Pond	15	NA	Town
Widgedon Pond	26	NA	Town

6. Plymouth PALS Program Description and Goals

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, begin to collect the new data, organize and evaluate old and new data, and provide feedback to citizens and town decision-makers about pond status and management concerns. The PALS program began by gathering water quality data on 40 selected ponds, organizing past data and comparing it to the collected data, sharing the data and comparisons through a Plymouth Pond and Lake Atlas, and working to continue this work beyond the initial MET funding. The Atlas has been made publicly available through the town's website and the town plans to update the Atlas on a regular basis, as new information become available. The Town will work with project partners, especially the pond associations, to share project findings in multiple settings and through various media outlets. The Town partnered with CSP/SMAST to help complete the Atlas, pond sampling and laboratory analysis.

Through the success of the PALS snapshots, the Town is expanding the PALS program to incorporate the development of pond management plans. These plans will include diagnostic assessments, listing and review of management options, and selection of a recommended option or set of options. Plan development will occur with a selected consultant or CSP/SMAST and will include targeted data collection needed to reliable understand and predict nutrient responses to management options. Targeted data collection will be determined by the physical characteristics of the pond (*i.e.*, depth, stream inflows or outflows, etc.) and need for sufficient information to understand the role of the component in the pond ecosystem function. Details of targeted data collection will be determined in coordination with the Town and based on procedures described in this QAPP. All management plans will be reviewed with pond association partners. Implementation of plans will occur based on Town prioritization.

6.1 Water Quality Monitoring Protocols for the Ponds

6.1.1. PALS Snapshot Sampling

As currently planned, Town of Plymouth staff will collect samples from the majority of ponds, while and some volunteers will each collect samples from remaining ponds. Town staff will work to maintain these sampling relationships in the future, but the total count and personnel/volunteers assigned to particular ponds may change depending on funding and personnel/volunteer availability. Since this is a snapshot sampling, each pond will be visited once during the August 15 to September 30 sampling period. Access is confirmed prior to the sampling period and, if required, prior to the day of sampling. Samples will be collected between 7 AM and 3 PM to maximize phytoplankton activity. The sampling period was selected in order to sample what is likely to be the worst nutrient related water quality conditions in the ponds. Individual sampling dates within the sampling period are based on sampler availability.

The sampling protocol requires locating the deepest location on the pond, collecting dissolved oxygen and temperature profiles (at 1 m depth intervals) at that location, measuring Secchi transparency, and collecting water quality samples at standardized depths. Dissolved oxygen and temperature profile readings are recorded using an YSI-85 meter (or similar) calibrated prior to each sampling event. Membranes or cartridges on the meter probe are changed according to recommendations in the meter operations manual. Sampling location GPS coordinates will be

determined for those ponds without prior sampling and past coordinates will be followed for those stations where coordinates have been determined previously.

The project sampling protocol requires that between 2 and 4 nutrient samples are collected at each pond, depending on water depth. A minimum of two samples are collected at each pond. If the pond is very shallow, two 0.5 m samples are collected. In moderately shallow ponds, at least two water samples are collected, one at 0.5 m and another 1 m off the bottom. If the pond is approximately 9 m deep, a third sample is collected at 3 m and if the pond is greater than 11 m, a fourth sample is collected at 9 m. This sampling protocol has been used for citizen-based, volunteer pond water quality PALS snapshots for 13 years on Cape Cod[2] and the consistency of this approach provides a potential valuable comparison between the ponds in the present study and other southeastern Massachusetts ponds that are in the same ecoregion.

All water column samples for water quality analysis are collected with Niskin samplers and sub-samples are transferred to dark HDPE acid-washed 1 liter bottles and transported in coolers with ice packs (4°C) to the Coastal Systems Analytical Facility at the School for Marine Science and Technology (SMAST), University of Massachusetts Dartmouth in New Bedford. Duplicate quality assurance (QA) samples will be collected and analyzed for 10% of samples collected during the PALS sampling period. All samples are delivered to the Analytical Facility within six (6) hours of collection. Laboratory procedures are described in the SMAST Coastal Systems Analytical Facility Laboratory Quality Assurance Plan (2003). Laboratory and field data collected, along with analyte detection limits and accuracy measurements, are shown in Table 2.

6.1.2. PALS Pond Management Targeted Sampling

The Town of Plymouth plans to move forward with prioritization of pond management plans and wants to ensure that all associated diagnostic assessments of the ponds have reliable data that can be used in regulatory settings. For this reason, the Town is including in this QAPP a series of anticipated data gathering techniques and accompanying review procedures that will apply to assessment of various components of pond and lake diagnostic assessments within the Town of Plymouth. These techniques will be refined during each individual pond and lake assessment, but each application will follow the basic characteristics of the approaches described in this QAPP.

Each of the associated techniques are described in attached Standard Operating Procedures (SOPs). The attached SOPs include the following assessment techniques:

1. Streamflow measurements
2. Sediment nutrient regeneration measurements

It is anticipated that other techniques will be added as individual ponds and lakes are assessed and their characteristics or ecosystem concerns and data gaps are identified.

6.2 Volunteer Monitoring

The majority of the ponds sampled during the initial round of the Plymouth PALS project were sampled by volunteers. Volunteers will represent various pond associations, homeowner associations, and other organizations that are partners in the Plymouth PALS program, as well as interested and willing residents. Most of the volunteer groups have years of experience with pond

[2] Eichner, E.M., T.C. Cambareri, G. Belfit, D. McCaffery, S. Michaud, and B. Smith. 2003. Cape Cod Pond and Lake Atlas. Cape Cod Commission. Barnstable, MA

sampling techniques. Town staff may accompany select volunteers to ensure consistency with sampling protocols.

6.3 Education, Outreach and Management

One of the primary goals of Plymouth PALS program is to engage and educate the community. PALS will expand to several watershed associations as well as smaller homeowner associations and areas where associations have not been developed. The Town will continue posting the Pond Atlas and updates on the website as well as distributing to watershed groups.

6.4 Schedules

6.4.1 Time Schedule of Plymouth PALS Water Quality Snapshots

TASK	DESCRIPTION	TIMELINE
2	QAPP	As soon as possible
3	Sampling and Lab Analysis	Sampling: August 15 through September 30 Lab Analysis Report: October 1 through Jan 30

6.4.2 Time Schedule of Plymouth PALS Diagnostic Assessments and Management Plans

The Town of Plymouth will schedule pond and lake diagnostic assessments and management plans as available funding allows. The Town will actively pursue grant funding opportunities to supplement Town funding.

7. Water Quality Test Parameters

All pond and lake water samples collected during Plymouth PALS Snapshots are tested by Coastal Systems Analytical Facility Laboratory at SMAST/UMassD campus in New Bedford, MA for parameters listed below:

1) Total Phosphorus
2) Total Nitrogen
3) pH
4) Alkalinity
5) Chlorophyll-a
6) Phaeophytin

Diagnostic assessments may include other parameters, such as: ortho-phosphorus, nitrate/nitrite-nitrogen, ammonium-nitrogen, and particulate organic nitrogen. CSP/SMAST Analytical Facility Laboratory is accepted for all the parameters listed in this QAPP via the SMAST Coastal Systems Analytical Facility Laboratory Quality Assurance Plan (2014), which included both fresh and salt water nutrient analysis. The CSP/SMAST Analytical Facility Laboratory typically completes over 30,000 chemical assays per year. Lab duplicates, blanks, and standards are completed according to the assay protocols (see attached lab SOPs).

PALS Snapshot and diagnostic assessment water samples are collected and maintained as outlined in Section 8 and the attached SOPs. All water samples are taken to the laboratory on the same day they are collected. The analysis is done according to MassDEP and/or US EPA criteria (See Table 1).

PALS Snapshot analysis results are submitted to Program Manager and Data Manager for review and comparison with previous PALS results. Pond management plans will include review and summary of all diagnostic assessment data. The Town anticipates that further review of PALS Snapshot results will occur during individual pond diagnostic assessments and management plans, as well as regular town-wide review over a number of Snapshots, PALS Snapshot results will be used as baseline against which to assess future data, for educational purposes, and in discussion of possible management efforts.

8. Data Quality - Quality Assurance

The Plymouth PALS Snapshots and diagnostic assessment for pond management plans will employ and satisfy the quality control measures and data quality objectives outlined in this section. The data collected through the both types of monitoring activities will be used in making decisions regarding management activities as described in the Program Description and Goals section. This section outlines measures to ensure samples are collected and analyzed properly, thereby meeting quality standards.

8.1 Data Representativeness

Data Representativeness will be met by the following requirements:

8.1.1. All PALS Snapshot sampling sites are selected to be representative of "average" late summer conditions for the water body or pollution source.

8.1.2. All diagnostic assessment samplings will be selected based on the characteristic of the measured matrix (*i.e.*, pond water, stream water, sediments, etc) and the characteristics of

the pond (*i.e.*, near shore, deep basin, etc). Diagnostic assessment monitoring will focus on summer as the primary water quality management period.

8.1.3. Any abnormal or episodic conditions that may affect the representativeness of sample data are noted and maintained as metadata.

8.1.4 Field blanks will be collected every sampling day and subject to all analysis procedures, including reporting, to ensure sampling and lab procedures are not adding bias to results.

8.2 Duplicate Sampling

8.2.1. Duplicate field samples are required for approximately 10% of samples for each sampling run. A unique identifier will be assigned to the duplicate and noted in the Survey Field Datasheet (Appendix I).

8.2.2. Duplicate samples are collected from the same sample collection. Duplicate PALS Snapshot samples are the filling of two 1L bottles from the same collection samplers. Duplicate samples in diagnostic assessments will vary depending on the parameter being assayed.

8.2.3. Upon receipt of field duplicate results, the QA Officer will review to ensure samples are within an acceptable range, normally $\pm$10% RPD.

8.2.4. Duplicate field readings will be taken for selected ponds for 10% of overall PALS Snapshot readings. For these selected ponds, profile readings for dissolved oxygen and temperature will be recorded according to specified procedures as the meter probe is lowered through the water column and then again at the same depths as it is raised through the water column. Duplicate Secchi readings will be completed in the same way.

8.3 Comparability of Project Data

The comparison of project data to previously collected data will be enhanced by the using the same protocols in PALS Snapshots and Diagnostic Assessments for Pond Management Plans.

8.3.1. Documenting sampling sites, times and dates and sample transport and transfer on Plymouth PALS Sampling Sheet (Appendix D), this also functions as a sample chain-of-custody form. No samples are accepted at the CSP/SMAST Analytical Facility Laboratory without a chain-of-custody form.

8.3.2. Comparability of data can be produced by following these established protocols. This will ensure that all new samples are collected following the same procedure and approach and are assayed by the same methods as in the prior surveys.

8.3.3. Results can be compared to historical data from that station collected during the same season. Diagnostic assessments will include data from seasons other than the late summer PALS Snapshots.

8.3.4. Detailed and complete sample records including the Plymouth PALS Snapshot Sampling Sheet and chain-of-custody forms (Appendix D) will be maintained.

8.3.5. Final reports detailing data and conclusions may be published and posted by the Town.

8.4 Completeness of Project Data

The ultimate goal for Snapshot and diagnostic assessment monitoring is to obtain acceptable measurements for all parameters and assays attempted. The number of planned measurements will vary depending on the ponds selected (planned Snapshot) or the type of diagnostic monitoring for a selected pond (*e.g.*, # of sediment sampling sites for 10 acre pond vs. a 100 acre pond). Completeness is gauged as the number of QA-passed measurements divided by the number of planned measurements times 100%.

The Tables below summarizes the accuracy/precision, the minimum detection limits, the approximate potential range, the analysis test methods and holding times from the CSP/SMAST Analytical Facility Laboratory. The Laboratory address is:

Coastal Systems Program
Attn: Sara Sampieri, Lab Manager (ssampieri@umassd.edu)
School for Marine Science and Technology
University of Massachusetts Dartmouth
706 South Rodney French Blvd.
New Bedford, Massachusetts 02744-1221
508-910-6325

Table 1. PALS Snapshot Water Quality Program and Pond-specific Diagnostic Monitoring, field parameters measured & data objectives					
Parameter	**Method/ Range Units**	**Sensitivity**	**Precision**	**Accuracy**	**Calibration**
Temperature	Thermometer -10°C to +100°C	0.5°C	<10% RFD (duplicate readings during up & down profiles)	1°C	Certified thermometer over temperature range
Dissolved Oxygen/Hach OX2P (ppm)	Modified Winkler Titration/ YSI Oxygen Meter	0.1 ppm	<10% RFD (duplicate readings during up & down profiles)	1 ppm	Simultaneous sample
Water Clarity	Secchi Disk disappearance/ meters	1 cm	<10% RFD (duplicate readings in up & down)	NA	NA: line is measuring tape
Pond-specific Diagnostic Monitoring only (will only be used if pond has diagnostic need)					
Streamflow: Water Levels	submersible pressure transducer and datalogger (described in attached SOP)	±0.1% (35°F to 70°F range)	<10% RFD (field depth measurements)	±0.2% (35°F to 70°F range)	Water level logger factory calibrated (regularly lab checked & cross-checked with field measurements)
Streamflow: Instantaneous velocity	electromagnetic velocity sensor (described in attached SOP)	±0.05 ft/s	<10% RFD (duplicate readings in selected sections)	±2%	Velocity meter factory calibrated (regularly checked as described in SOP)

Table 2. 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 CaCO3	0.5	80-120% Std. Value	Acid Titration [1]	6 hrs	10%	5%	5%
Chlorophyll *a*/ Phaeophytin *a*	µg/l	0.1	80-120% Std. Value	Acetone extraction [2]	24 hrs	5%	5% + after any sample off scale	5/day minimum
Nitrogen, Total	µM	0.06	80-120% Std. Value	Persulfate digestion [3]	Frozen 60 days	10%	2/sample set	10%
pH	stnd units	NA	±0.2 of QC standard	Electrode [4]	6 hrs	10%	5%	5%
Phosphorus, Total	µM	0.1	80-120% Std. Value	Persulfate digestion [5]	Preserved 60 days	5/sample set	5% + after any sample off scale	5/day minimum

Notes:

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)

b) For accuracy determination, comparison of spike samples and known standards is preferred.

c) Overall precision is measured using the Relative Percent Difference, RPD (or std. deviation for n > 2) of field duplicate samples. Lab precision is based on an estimate of the RPD between duplicate aliquots of the same lab sample.

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.

e) Lab duplicates, blanks, and spikes are based on assay SOPs (see attached in Appendix F)

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 19th 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.

9. Sampling Procedures

All sampling processes begin the day before field sample collection, by ensuring all required instruments and supplies are gathered. Checklist of required supplies includes the number of sample bottles and chain of custody/data sheets required for the next day. Sample bottles, including bottles for QA/QC duplicates, ice packs, coolers, and meters will be reviewed. Bottles must be acid-leached, 1L, dark Nalgene bottles. Bottles will be acid-cleaned (HCl), distilled water-rinsed and dried no more than one week prior to sampling.

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. Diagnostic assessment sampling locations are determined based on the matrix to be sampled (i.e., sediments, stream water) and the details of the pond or, in the case of a stream, a well-constrained measurement point close to the pond. 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 (Appendix D) for all PALS Snapshot samplings. For diagnostic assessment sampling sites, GPS coordinates will be determined for all samples, recorded in field notebooks, and summarized in the resulting pond management plan report.

Pond diagnostic sampling procedures are described in the attached SOPs. Water column sampling procedures for the diagnostic sampling generally follow the same procedures for PALS Snapshots in order to ensure comparability of results. 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. Care is taken to record these readings on the opposite side of the boat from the Secchi readings in order to minimize any potential anomalies caused by sediment disturbance during the total depth recording. 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. Samples will be collected from

surface to bottom with a rinse of the sampler with surface water between each depth; distilled water will be used to rinse the sampler after collection of the deepest sample. 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 with distilled water, 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_2SO_4) 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.

10. Training of PALS Snapshot Volunteers

Prior to the start of the sampling period (August 15), Town personnel will conduct individual training for all involved sampling personnel and volunteers. This will include stressing consistency of sampling techniques and will review sampling protocols, equipment use, sampling handling procedures, sampling safety, and provide suggested pre-sampling checklists.

11. Safety Considerations

CSP/SMAST and town field staffs are professional, experienced water quality samplers and have extensive experience launching and utilizing boats and sampling equipment. Sampling is generally done with two staff people. A separate CSP/SMAST staff member is contacted on departure and return of the field team with set deadlines for return. Similar procedures will be stressed to the volunteer samplers. Every effort is made to ensure safe access to each pond.

12. Documentation and Records

The Plymouth PALS program generates records and documents related to field data collection, data processing, and planning. The Snapshot water sampling test results are compiled in Excel spreadsheets, which are submitted to the Town and maintained at CSP/SMAST. CSP/SMAST maintains documentation and records related to both PALS Snapshots and any data generated by CSP/SMAST for any diagnostic assessment/pond management plans that CSP/SMAST conducts or provides assistance. Town maintains records of all community outreach and coordination associated with the PALS program. Electronic records including spreadsheets, digital photographs, notes, and reports are maintained collectively by CSP/SMAST and the Town.

The Plymouth PALS QAPP will be periodically updated based on planned Town activities, including both Snapshot sampling and diagnostic assessments/management plans. The Town and CSP/SMAST will maintain copies of the QAPP and the Town will address any minor changes with MassDEP.

13. Project Oversight, Data Verification and Validation Procedures

The Project Manager will oversee the sampling project and ensure data verification and validation procedures are completed. The Quality Assurance Officer/Data Manager will provide on a yearly basis laboratory and field results in a spreadsheet format with Quality Assurance and Control Data. Any laboratory results outside of the QAPP thresholds will be highlighted and noted as such. The Project Manager will review this data and add on a separate sheet the breakdown of Quality Control including but not limited to duplicates and equipment calibrations. The Project Manager will upload the data in spreadsheet format onto the Town of Plymouth's Pond Data website as well as provide a copy to the Department of Environmental Protection.

Appendix A – Plymouth PALS Snapshot Water Sampling Procedures

1.0 Purpose

The purpose of this procedure is to describe the field methodology the collection of surface water samples for the Plymouth Pond and Lakes Stewardship (PALS) Snapshots by the Town of Plymouth (Town) and the Coastal Systems Program, School for Marine Science and Technology, UMass Dartmouth (CSP/SMAST).

2.0 Definitions

Surface water: Includes all water on the surface of the ground directly exposed to the atmosphere, including, but not limited to, lakes, ponds, reservoirs, artificial impoundments, streams, rivers, springs, seeps, and wetlands.
YSI: Yellow Springs Instrument to collect field water quality parameters.

3.0 Sampling Locations

Preliminary sampling locations will be determined and evaluated prior to the start of sampling. Final sampling locations of each pond's deep basin will be identified by GPS coordinates.

4.0 Procedure

4.1 Equipment

- map of sampling locations
- field monitoring/sampling/chain of custody sheet, clipboard and #2 pencils
- Niskin sampler, to collect water samples at depth
- Secchi disk
- D.O. probe and meter (YSI-85 or equivalent)
- GPS
- Acoustic depth sounder
- sample bottles with labels
- waterproof permanent marker for bottle labels
- sampling gloves for each site
- cooler with ice packs
- Nalgene bottle filled with distilled water for rinsing of Niskin sampler
- safety items; cell phone, first aid kit and safety vest (for boat)

4.2 Sampling Method

Arrive at sample site and record applicable information in field monitoring/sampling chain-of-custody sheet. Label the sample bottle with appropriate site name, date and time of sample collection.
Collect field data, including Secchi/clarity, temperature/dissolved oxygen profiles and total water depth. Collect water samples according to depth of the pond. Record pond name, depth, and date on each sample bottle and record corresponding information on the field monitoring/sampling chain-of-custody sheet along with time of day.

4.3 Field Duplicate Collection

Field duplicates will be taken based on 10% of samples taken per year or once each sampling run. For example, 40 locations per year would require 4 duplicate samples. The Project Managers will determine duplicate location sites. The field monitoring/sampling chain-of-custody sheet will note the collection of a duplicate sample.

Appendix B – Plymouth PALS Water Sampling Procedures*: Field Checklist*

Pond Monitoring Program Checklist

Needed prior to sampling date:

- Ensure adequate bottle supply for all anticipated samples, including field duplicates
- Ensure all sampling equipment is working properly.
- Gather all ancillary field materials, including GPS, sampling sheets, cooler, ice packs, labeling pen, etc.

For sampling day:

- Field monitoring/sampling chain-of-custody sheets for each pond
- Map(s) or queued digital map images of access points
- Phone numbers of access contacts for private access points
- Sufficient sample bottles for each pond plus field duplicates
- Cooler and ice packs
- Sampling equipment, including DO/Temperature meter, sampling device, and Secchi disk

Return of samples to lab:

- Ensure samples remain cold until returned.
- Samples should be returned to lab within 6 hours of collection to maintain holding times.
- Field monitoring/sampling chain-of-custody sheets should be signed by samplers, transfer personnel, and all CSP/SMAST staff that control/transport the samples/data sheets, including time and location.
- Ensure field monitoring/sampling chain-of-custody sheets are collected and stored for later review and input of field data into spreadsheets.

Appendix C – Plymouth PALS Water Sampling Procedures*: Field Instructions*

Plymouth PALS Ponds Sampling Procedures

1. Record all applicable information on the Plymouth PALS Snapshot field monitoring/sampling chain-of-custody sheets, including sampling staff, date, weather conditions, and sampling depths.
2. Collect Secchi reading and total station depth; record readings on monitoring/sampling sheet. If the pond is selected for duplicate Secchi readings by the Town coordinator (noted to volunteers at the time of instrument pickup), procedures for a Secchi reading will be completed twice. Duplicate Secchi readings will be recorded on the monitoring/sampling sheet.
3. Collect dissolved oxygen and temperature profile readings at 0.5 m, 1 m, 2 m, and subsequent one meter increments to within 0.5 m of the bottom; record readings on monitoring/sampling sheet. If the pond is selected for duplicate profile readings by the Town coordinator (noted to volunteers at the time of instrument pickup), readings will be collected at the same depths as the probe is raised from the deepest increment to the shallowest increment. Duplicate profile readings will be recorded on the monitoring/sampling sheet.
4. Enter pond name, date and sample depth on sample bottles.
5. Collect water samples at depths specific to the total station depth. A minimum of two samples per pond with samples at 0.5 m and 1 m off the bottom. If the pond is 1 m or less in depth, collect two 0.5 m samples. In ponds of ~9 m, collect one additional sample at 3 m depth. In ponds with a total station depth greater than 11 m, collect one additional sample at 9 m depth. Record sampled depths on monitoring/sampling sheet.
6. Samples should be transferred to 1L dark, acid-washed, Nalgene bottles. Care should be taken to avoid contact with the interior portion of the bottle or with the water stream between the sampling device and the sample bottles.
7. Sample bottles should be stored in the cooler as they are collected.
8. Duplicate sample for each sampling run should be randomly collected and recorded on appropriate sampling sheet.
9. Samples should be returned to the CSP/SMAST lab within 6 hours of sampling to ensure holding times are met.

Appendix D – Plymouth PALS Ponds Sampling Program field data/sampling chain-of-custody sheet

SMAST University of Massachusetts Dartmouth

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. Intermit. Rain

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

Plants on Pond (check conditions):	Over 50%	25% to 50%	10% to 25%	up to 10%	less than 1% or None
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

DISSOLVED OXYGEN/TEMPERATURE PROFILE

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.).

Depth (m)	Temp (°C)	Dissolved Oxygen (mg/l)	Depth (m)	Temp (°C)	Dissolved Oxygen (mg/l)	Depth (m)	Temp (°C)	Dissolved Oxygen (mg/l)

COMPLETE BOTH SIDES OF DATA SHEET

LAKE/POND NAME: _____

GPS Coordinate: _____

Sample Collector: _____ Date: _____

WATER QUALITY SAMPLING

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

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

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

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

⇒ 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. **Please call Kim Tower 774-244-0236** to either notify what time you will be delivering to town hall (before 2pm) or to have a pick-up samples/equipment. You will need to relinquish samples to the Town (signature below). Kim will deliver to the Coastal Systems Program/SMAST lab the same day (prior to 3:30 PM)!

Coastal Systems Program/SMAST lab is at 706 South Rodney French Blvd., New Bedford, Massachusetts 02744-1221, 508-910-6314.

SAMPLE SIGNOFFS

	Signature	Received	Delivered
		Date/Time	Date/Time
Pond Sampler			
Town - Deliverer			
Lab Analysis			

COMPLETE BOTH SIDES OF DATA SHEET

Appendix E – Plymouth PALS Ponds Diagnostic Assessment Procedures for Pond Management Plans

Listed Procedures:

1. Streamflow measurements
2. Sediment nutrient regeneration measurements

Streamflow Measurement and Stream Water Quality Sampling
Standard Operating Procedures for Town of Plymouth
Pond and Lake Diagnostic Assessments/Pond Management Plans
April 2020

Objective

Any Town of Plymouth ponds and lakes developing a pond management plan shall measure streamflow and contaminant loads into and/or out of ponds for at least one year based on the procedures described in this SOP. Data collection shall be concentrated during the primary management period (April to October) and less frequent during other months.

Background

The Town of Plymouth largely overlays a largely unconfined, groundwater aquifer where streamflows tend be a mix of surface expressions of groundwater and drains of higher elevation groundwater upstream. As such, streamflow tends to fluctuate with seasonal groundwater fluctuations, but can also be impacted by shorter term events, such as rainstorms, and longer term trends, such as multi-year high groundwater conditions. Analysis of streamflow results should try to address these fluctuations as well as annual fluctuations. It is anticipated that streamflows into or out of selected ponds to utilize this SOP will mostly be the first streamflow readings ever recorded for these streams.

Procedures

Town staff and contractors completing Pond and Lake Diagnostic Assessments/Pond Management Plans for the Town of Plymouth shall utilize the following procedures to record stream inflows and outflow readings to the selected pond or lake and collect, process, and prepare stream water quality samples for parameters specified in the scope of work.

Cross-sectional stream velocity readings and cross-sectional areas shall be measured biweekly between April and October and at least monthly during other months at selected stream measurement locations. A continuous water level recorder that records water level readings every 10 to 15 minutes will also be installed at the stream measurement location. A Marsh McBirney Flow-mate Model 2000 or equivalent current meter will be used to measure stream velocities during each site visit. Stream water levels will be measured using a Global Waters Water Level Logger: WL-15 or equivalent. The gauges will be vented to the atmosphere.

The techniques described in this SOP are routinely utilized by staff at the Coastal Systems Program at the School for Marine Science and Technology, University of Massachusetts Dartmouth (CSP/SMAST). Personnel using this SOP should have training and field experience in making stream-gage site visits, recording and documenting pertinent flow data and collection of stream water quality samples. Personnel should also have familiarity with other relevant Town of Plymouth Pond and Lake Diagnostic Assessments/Pond Management Plans SOPs.

No single procedure will be applicable to all sampling situations; therefore, the selection of the sampling site will include judgments based on criteria that would produce the most representative stream water quality sample and flow measurement, and including consideration of safety, efficiency, and site access/ownership. Additional site considerations shall include: unchanging natural control, streambed free of aquatic growth and relatively smooth, generally straight channel,

flow that does not go dry during low flow periods, stable channel cross-section, and no influence of backwater effects (culverts, dams, confluences).

Equipment

- field monitoring/sampling/chain of custody sheet, clipboard and #2 pencils
- field data sheet
- D.O. probe and meter (YSI-85 or equivalent)
- acid leached 60 ml polyethylene bottles with labels
- acid leached 1 L polyethylene bottles
- waterproof permanent marker for bottle labels
- sampling gloves for each site
- cooler with sufficient ice packs
- safety items; cell phone, first aid kit
- tape measure
- top setting wading rod
- Marsh McBirney Flow mate 2000 velocity meter or equivalent; properly calibrated
- Global Waters Water Level Logger: WL-15 or equivalent vented water level logger with probe and cable, PVC tube, weight, and other materials for installation
- Laptop or other similar data storage unit for monthly download of water level logger data

Stream Cross Section and Velocity Measurements:

Permanent markers will establish the cross-section stream velocity location. A measuring tape will be manually stretched across the width of the stream channel and, while facing up-stream, the left and right banks of the channel will be noted in feet using the measuring tape. The transect will be marked with permanent markers to which the tape measure will be affixed on each sampling occasion. Water depth across the width of the stream will be measured in 0.5 foot increments using the top setting wading rod. Water depth will be measured in meters. Total stream channel cross sectional area will be the summation of the total number of segment cross sectional areas. The summation of the products of stream subsection areas of the stream cross-section and the respective measured velocities will represent the computation of stream flow (Q). A rating curve will be developed for each gauge to transform level data to discharge rates. Measurement details will be recorded in a field record book in order to maintain a record of changes in the channel bottom or bank characteristics.

Stream water velocity measurements will be taken, at a minimum, each time the water level logger data is downloaded. Additional velocity measurements may be taken in between instrument downloads depending on weather conditions in order to capture high or low flow events. Water quality samples will be collected on each visit to the gauge site. Water quality sample parameters will match those collected in the pond, as determined by the scope approved by the Town.

Field data sheet for collection of velocity data have been developed (see below) and will be used to record velocity measurements, stream depths, and distance from the right or left bank where a velocity measurement is taken. In the absence of a field sheet, the same information can be recorded in a field notebook (as used by the USGS).

Field data collected for each specific stream being profiled will include:

- Name of the pond or lake receiving the stream discharge

- Name of the stream/river being profiled
- Name of the person doing the velocity measurements and those assisting
- Date/time
- Weather conditions (clear, fog, cloudy, drizzle, intermittent rain, rain, snow, etc.)
- Left bank distance in meters (facing upstream)
- Right bank distance in meters (facing upstream)
- Distance from bank where velocity measurement is being taken
- Velocity (m/s)
- Depth (meters)
- Height of water above water level logging probe (meters)
- Staff gage measurement (where available)
- Nutrient sample collection (sample ID)

The velocity meter used for Plymouth Ponds stream monitoring will be the Marsh McBirney Flow mate 2000 velocity meter or equivalent. The velocity meter is factory calibrated, but the calibration shall be regularly checked. If CSP/SMAST is conducting the monitoring, the velocity probe will be checked using a test tank containing still water. The velocity meter probe is mounted on a sled that runs the length of the test tank at a constant speed. The speed of the sled is varied in order to check the velocity meter function at low, medium, and high flow rates. Sled runs should be conducted at speeds that capture the range of flow rates that are encountered in the field program. Four sled speeds have been traditionally used in previous CSP/SMAST velocity meter calibration checks: 2.0 cm/s, 20 cm/s, 40 cm/s, and 80 cm/s. Multiple repetitions at a selected sled speed are performed beginning at the lowest speed then increasing incrementally. A three to ten minute time interval is typically used between runs to allow the water in the test tank to return to still conditions. Potassium permanganate is introduced to the tank between the runs at higher speeds to check that the water in the test was sufficiently still to begin the next run. After the highest speed is run, the lowest speed is rerun to check that instrument drift is not occurring. If a drift of more than 5% is encountered the instrument is sent back to the manufacturer for maintenance.

Stream Flow Calculation:
Determination of stream flow will be calculated and based on the measured values obtained for stream cross sectional area and velocity (Rantz *et al*. 1982). Stream discharge will be represented by the summation of individual discharge calculations for each stream subsection for which a cross sectional area and velocity measurement were obtained. Velocity measurements across the entire stream cross section WILL NOT be averaged and then applied to the total stream cross-sectional area.

Each stream subsection will have a calculated stream discharge value and the summation of all the sub-sectional stream discharge values will be the total calculated discharge for the stream. The formula that will be used for calculation of stream flow (discharge) is as follows:

$$Q = \Sigma(A * V)$$

where:
Q = Stream discharge (m3/day)
A = Stream subsection cross sectional area (m2)
V = Stream subsection velocity (m/s)

Water quality parameter discharge is calculated using the paired discharge and concentration data to determine the mass flux through the gauging site. These data are expressed as parameter mass per unit time (kg/d). The mass flux over the period of interest (month, season, year) is determined by integrating the area under the appropriate interval of the daily mass flux versus date graph.

Stream Water Level Measurements:
The factory calibrated water level loggers will be deployed for continuous measurement of water levels; these readings will be transformed into flow estimates based on the rating curve developed for each site from the flow/stage data. The water level loggers will be prepared in the laboratory for deployment in selected streams by checking that the instrument is properly sealed to prevent malfunctions resulting from moisture build up in the instrument casing. Deployments will typically be continuous for approximately one year.

Continuous water level recorder will be a Global Water Water Level Logger: WL-15 or equivalent. The recorder will be programmed to record water level readings at least every 15 minutes. The gauge will be vented to the atmosphere. Water level loggers are factory calibrated prior to the start of the installation. The function of the probe is field verified each time a velocity profile is being run by measuring the height of water over the probe with a measuring tape and comparing the manual measurement with the instrument measurement. Manual measurements are subsequently plotted against instrument measurements and simple linear regression analysis is performed on the data to determine the linear relationship. The calibration is acceptable if the $r2 > 0.98$.

The water level instrument will typically be encased in a PVC tube, open ended on the bottom so that the instrument cable can run freely and capped on the top so that moisture cannot degrade the instrument communication port. The PVC-encased instrument will be mounted to a convenient and permanent natural or artificial structure and the water level probe held in the desired location in the stream reach using either a stilling well or placement on a flat weight (ca. 40 lbs) in shallow streams. The instrument cable will be run as unobtrusively as possible so as to be hidden from view and to not become an obstacle. The water level probe will be placed at the deepest point in the stream channel so as to remain submerged during low flow seasons and mean sea level will be used as the vertical datum to which the probe is referenced. The water level probe will be weighted down appropriately so as to prevent the probe from migrating downstream during increased flow rates.

Water level data will be downloaded monthly in the field via laptop computer. Water level data will be field verified each month against either an in-stream surveyed staff gage or by making a manual water level measurement of height of water over the water level probe using a tape measure. Measured height of water over the in-stream water level probe will be compared to water level data record to confirm that data record is comparable.

Stream Water Quality Samples
Water samples from flowing surface waters should represent the flow in the stream, and not simply conditions that might occur in a small portion of the cross-section. Sampling selection should be based on access to a well-mixed, flowing portion of the stream, and the ability to pull water from below the surface without disturbing bottom sediments. Under no circumstances are samples to be collected from standing or stagnant water. If there is no discernable flow, no sample shall be collected. Flow measurements shall be collected each time water quality samples are collected.

Contractors must utilize laboratories qualified to complete water quality assays specified in the Town of Plymouth Pond and Lake QAPP. Contractors are expected to work directly with appropriate labs for specific instructions on bottle rinsing, sample preservation, bottle labeling, and submission instructions. The CSP/SMAST Coastal Systems Analytical Facility Laboratory will be considered qualified for analysis the parameters specified in the Town of Plymouth Pond and Lake QAPP.

Reference

Rantz, S.E. and others. 1982. Measurement and computation of streamflow. Vol 1: Measurement of stage and discharge (313 pp.). Vol 2. Computation of discharge (373 pp.). US Geological Survey Water-Supply Paper 2175.

Watershed / Embayment: _____
Stream / Creek: _____
Gauge ID.: _____
Date: _____
Time: _____
Personnel: _____
Signature: _____
Gauge Data Downloaded (y/n): _____

Height of Water above Transducer (cm): _____

Nutrient Sample (y/n): _____ Sample ID: _____ Sample Depth: _____

Parameters	Section 1	Section 2	Section 3	Section 4	Section 5	Section 6	Section 7	Section 8	Section 9	Section 10
Velocity (cm):										
Measurement Depth (cm):										
Total Water Depth (cm):										
Total Width (cm):										
Notes:										

Pond and Lake Sediment Nutrient Regeneration Measurements
Standard Operating Procedures for Town of Plymouth
Pond and Lake Diagnostic Assessments/Pond Management Plans
April 2020

Objective

Any Town of Plymouth ponds and lakes developing a pond management plan shall have sediment samples collected and incubated to measure nutrient regeneration under various redox conditions as specified according to this SOP.

Background

Water column nutrient concentrations in ponds are the combination of watershed inputs (*e.g.*, septic systems, stormwater runoff, lawn fertilizers, etc.) and inputs from the sediments within the lake. Pond or lake sediment inputs are increased during the summer by warming of sediments and/or their isolation in deeper, stratified ponds. These sediment nutrients are previous years watershed inputs and their summer release back into the water column (*i.e.*, regeneration) is usually prompted by loss of dissolved oxygen. Phosphorus, usually the primary nutrient driving plant growth in lakes and ponds, is released at different rates from the sediments as dissolved oxygen decreases. Collection of intact sediment cores and their incubation testing response to gradually reduced dissolved oxygen concentrations provides a direct measurement of the quantity of phosphorus release and the dissolved oxygen conditions causing the release. Failure to accurately account for sediment regeneration will result in unreliable pond water quality management strategies.

Procedures

Town staff and contractors completing Pond and Lake Diagnostic Assessments/Pond Management Plans for the Town of Plymouth shall utilize the following procedures to measure phosphorus and nitrogen regeneration from pond and lake sediments for parameters specified in the scope of work.

Personnel using this SOP should have training and field experience in collection of underwater sediment cores, incubation procedures, recording and documenting pertinent core collection and incubation data and synthesis of resulting incubation results. Personnel using this SOP should have familiarity with other relevant Town of Plymouth Pond and Lake Diagnostic Assessments/Pond Management Plans SOPs.

The techniques described in this SOP are routinely utilized by staff at the Coastal Systems Program at the School for Marine Science and Technology, University of Massachusetts Dartmouth (CSP/SMAST). The sediment regeneration program uses accepted methods for low level analysis in saltwater, but have also regularly been used in freshwater as well. These methods are accepted by the best marine research laboratories in the United States. EPA or Standard Methods techniques are employed by the CSP/SMAST laboratory when available. All methods have been inter-calibrated with a variety of methods and with various certified laboratories (freshwater only) and marine laboratories.

Equipment

- All appropriate SCUBA diving equipment (as specified in certified safe diving protocols)
- Core containers (15 cm ID), magnetic stirrers, core stoppers, baffles, coolers/incubation containers, carboys (or equivalent water containers), water filters, etc.
- Orbisphere meter and probe
- timer
- field monitoring/sampling/chain of custody sheets, clipboard and #2 pencils
- field data sheet
- D.O. probe and meter (YSI-85 or equivalent)
- Secchi disc
- acid leached 60 ml polyethylene bottles with labels
- acid leached 1 L polyethylene bottles
- waterproof permanent marker for bottle labels
- sampling gloves for each site
- cooler with sufficient ice packs
- safety items; cell phone, first aid kit

Sediment Core Collection

The concept in determining sediment nutrient regeneration rates is to collect an undisturbed sediment sample and incubate it under *in situ* conditions to allow natural exchange of nutrients between the sediment and overlying water under controlled conditions. Temperature control is maintained through mixed circulating water baths and constant temperature monitoring. Bottom water (1-2 meters above bottom) is collected by submerging a 20 liter acid leached polycarbonate container from the region of each core site. The container is capped and returned to the field laboratory, filtered (ca. 1 um) and used to replace the headspace water of the flux cores prior to incubation. The water overlying the sediment is gently mixed with a magnetic stirrer and the headspace is sealed with a gas-tight closure fitted with sampling ports during incubation.

Core collection in freshwater ponds and lakes is targeted for April to try to minimize low oxygen impacts on sediment nutrient regeneration to the water column. In order to determine water column nutrients, potential particle settling, and establish a pre-summer management period baseline, nutrient samples are collected throughout the water column 1 to 2 days prior to the core collection, on the day of core collection, and 1 to 2 days after the core collection. A minimum of three cores will be collected from each pond or each pond basin depending on the bathymetry, inflow locations, and the lake volume.

Benthic nutrient flux cores are collected by SCUBA diver and maintained at *in situ* temperatures until returned to the laboratory (both on the boat and at the shore-side location). Baffles and appropriate anti-mixing procedures are used during the transport of the cores following shore-side incubations. While much effort is generally spent in achieving highly accurate chemical assays (accuracy to 1%) to determine flux rates, handling of the sediment cores themselves (the source of the fluxes) is generally not well controlled and yet can create several fold errors in rates. In fact, CSP/SMAST long experience in these measures in a variety of sediment systems indicates that core handling can be a major source of error in benthic nutrient flux measures. For these reasons, incubations are conducted at a shore-side site to avoid overland transport of sediment samples.

The CSP/SMAST laboratory has all of the equipment and personnel required for core collection, shore-side incubations, and laboratory incubations.

Sediment Core Incubation

Upon arrival at the nearshore field laboratory sediment cores are inspected for any surface disturbance or large fauna (*e.g.*, mussels or fish) which would cause rejection of these cores. Acceptable flux cores are then sealed from the atmosphere with machined core tops fitted with magnetic stirrers that gently mix the overlying water without disturbing the sediment surface. Oxygen will be determined using an Orbisphere meter and electrode (the probe fitted through an opening in the core top) calibrated at 100% and 50% of atmospheric equilibration at the temperature and salinity of the headspace water of the cores. The headspace of the cores from each of the seven stations will be replaced with 0.22 micron filtered water (collected from each core site). Subsamples of the filtered water will be incubated to control for oxygen and nutrient changes in the headspace not associated with sediment flux. In all cases the incubation will continue until a significant flux is detected or to 36 hours. A "significant flux" is defined as one where the least-squares regression of the headspace analyte concentration over time has a slope different from zero. The headspace will be set so as to maximize the signal and minimize the incubation time (ideally 18 hours).

At least four to five time points (plus time zero) will be conducted per core incubation. Dissolved oxygen will not be allowed to decline to less than 50 percent of air equilibration. Since oxygen disappearance rates may exceed those of other solutes, we will continue the incubations after completion of the oxygen uptake assay by aerating the headspace until the solute flux assays are completed. At each measurement time point, headspace water will be removed through a port in the gas tight headspace with equal replacement with the setup water; samples are immediately filtered (Millipore 0.22 micron in-line filtration) into acid leached 60cc polyethylene bottles upon removal (Table 1). This approach allows water removal without even brief pressure changes to the headspace (negative pressures can increase fluxes in some incubation systems). A minimum of 4 samples will be collected for each time point. All fluxes will be adjusted for water removals and measured activities within the headspace water.

Ammonium, nitrate + nitrite and ortho-phosphate and dissolved organic nitrogen (and oxygen) will be analyzed for each of the time point sample volumes. Temporal changes in headspace concentrations will be used to calculate phosphorus and nitrogen flux rates. The time-course measures will be used to ensure calculations from linear increases. Samples for ammonia, nitrate/nitrite, and phosphate will be analyzed against reference standards having nutrient concentrations bracketing those of the samples. Standards will be analyzed daily, and checked for linearity ($r^2 > 0.99$) and acceptability of blanks. All standards and blanks are run in duplicate. The dissolved oxygen meter will be calibrated against air-saturated water and the calibration will be checked prior to each oxygen measurement. Deviations from 100% saturation will be noted and appropriate corrections will be applied to the data following the manufacturer's manual. Nutrient samples will be analyzed in conformance with the same standards as applied to the PALS Snapshot water quality monitoring and stream SOP.

Minimum performance criteria are listed in Table 2, although the methods used in the program generally exceed these minima. The acceptable criteria for field blank cleanliness is generally a

reading less than the detection limit. In occasional instances where high sensitivity methods are employed, the field blank must be less than 10% of the sample value.

Table 1. Sediment Regeneration, Nutrient Parameters				
Parameter	Sample Volume/ Container	Maximum Holding Time	Field Processing/ Preservation	Units
Nitrate + Nitrite	60 ml polyethylene acid-washed	28 days (frozen)	Field filter, store dark in lab -20 °C	µg/L
Ammonium	60 ml polyethylene acid-washed	24 hours (4 °C)	Field filter, store on ice in dark	µg/L
Orthophosphate	60 ml polyethylene acid-washed	24 hours (4 °C)	Field filter, store on ice in dark	µg/L
Dissolved organic N	1 L polyethylene acid-washed	24 hours (4 °C)	Field filter, store on ice in dark	µg/L
Dissolved Oxygen	none	none	Direct DO Meter Assay	mg/L

Table 2. Minimum Objectives for Sediment Regeneration Parameters				
Parameter	Field Precision	Laboratory Precision	Accuracy	Detection Limit
Nitrate + Nitrite	<20% RPD	<10% RPD	85%-115% of matrix spike	0.25 µM
Ammonium	<20% RPD	<10% RPD	85%-115% of matrix spike	0.25 µM
Orthophosphate	<20% RPD	<10% RPD	85%-115% of matrix spike	0.1 µM
Dissolved organic N	<20% RPD	<10% RPD	85%-115% of matrix spike	1 µM
Dissolved Oxygen	± 0.25 mg/L	± 0.1 mg/L	1% of air equilibration	0.2 mg/L
Temperature	± 0.25 °C	± 0.1 °C	± 0.2 °C	-10 °C – 40 °C
Salinity	± 0.2 ppt	± 0.1 ppt	± 0.2 ppt	0.3 ppt

Sample analyses should be performed for parameters by the Coastal Systems Analytical Facility at SMAST or a laboratory with similar QA procedures and assay capabilities. Samples are transported to the laboratory in coolers on ice. The methods employed are the standard methods of research level environmental laboratories. The methods used by the Coastal Systems Analytical Facility at SMAST have been through many EPA and other agency reviews as part of QAPP procedures over the past 20 years (5 years at CSP/SMAST, 15 years Woods Hole Oceanographic Institution).

All samples should have appropriate chain-of-custody (COC) procedures. All samples collected for nutrient analysis during core incubation are labeled in the field with Pond name, Town name, Sediment core, Sample ID, date (m/d/y), time of collection, and any other specialized information. Identical information is recorded on a data sheet/chain of custody, which also include notes as to environmental conditions, problems encountered, names of personnel, etc. Samples are all held on ice in coolers from collection through transport to SMAST Coastal Systems Laboratory.

If the SMAST Coastal Systems Laboratory is utilized, samples are logged-in upon delivery to the SMAST Coastal Systems Laboratory based upon field logs and COC forms prior to signature by

the authorized laboratory staff member. SMAST staff are on-call 24 hours when field teams are sampling, both to assist in any sample handling issues which might arise and to allow drop-offs and assay within the proscribed holding times. During log-in, sample integrity and clarity of labelling are checked and any unusual sample characteristics (identified by visual inspection or information from sample courier) are noted on the COC and in the appropriate laboratory notebook. All frozen and/or archived samples are stored in a freezer (-20°C) accessible only to authorized laboratory personnel. The laboratory analysts are responsible for the samples from arrival to analysis and data entry. Copies of the sample list, COC's and data sheets are made and kept by the CSP/SMAST laboratory.

Appendix F – Plymouth PALS Ponds CSP/SMAST Laboratory Assay SOPs

Listed Procedures:

1. Total Nitrogen/Total Dissolved Nitrogen
2. Nitrate+Nitrite
3. Total Phosphorus/Total Dissolved Phosphorus by Acid Persulfate Digestion
4. Chlorophyll a & Pheophytin a
5. pH & Alkalinity
6. Dissolved Oxygen
7. Temperature

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 μm 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 uL

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 μ 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+Nitrate 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 uM, 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:
% Recovery = ((x(a) – x(0))/ 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 μM.

References

Standard Methods for the Examination of Water and Wastewater. 19th 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 ($NO_{3+}NO_2$) 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 μm 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 KNO_3 (Fisher Number P263-500)
Sodium Nitrite $NaNO_2$ (Fisher Number S347-500)
Sodium Chloride NaCl (Fisher Number S271-3)
Magnesium Sulfate $MgSO_4 \bullet 7H_2O$ (Fisher Number M63-500)
Sodium Bicarbonate $NaHCO_3$ (Fisher Number S233-500)
Ammonium Chloride NH_4Cl (Fisher Number A661-500)
Sodium Hydroxide NaOH (Fisher Number S318-1)
Phosphoric Acid H_3PO_4 (Fisher Number A242-212)
N-(1-naphthyl)-ethylenediamine dihydrochloride (NED) (Fisher Number LC17550-1)
Sulfanilimide 4-$NH_2C_6H_4SO_2NH_2$ (Fisher Number O4525-100)
Hydrochloric Acid HCl (Fisher Number $A144^C$-212)
Copper Sulfate $CuSO_4 \bullet 5H_2O$ (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 Omnion 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 (uM) = $\frac{\text{(absorbance – intercept)}}{\text{slope}}$

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_2 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 with 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_3 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))/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, 19th 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 uL, 100-1000 uL

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 mmborosilicate test tubes

Preparation of Samples
1. For total P, samples are unfiltered; for Total Dissolved P, samples are pre-filtered with a 0.22 μ 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_4 standard to a sample
   % Recovery = ((x(a) – x(0))/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 μM.

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 μM.
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, 17th 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 μ 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 $MgCO_3$ (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 μ 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 $\mu g/cm^3$.

References

Standard Methods for the Examination of Water and Wastewater, 17th 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 $CaCO_3$/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 $CaCO_3$/L

Reference:

Standard Methods for the Examination of Water and Wastewater, Method 2320-B, 19th 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 $MnSO4 \bullet H2O$ (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 uM O_2 (i.e. 2.782 on the display = 278.2 uM 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 μM

References

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

TitraLab™ 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 pyncnocline.

Equipment:

Standard Celsius mercury-filled field thermometer with a range of -5°C to +40°C, a precision of ± 0.5°C and an accuracy of 1°C.
Standard thermister with a range of -5°C to +40°C, a precision of ± 0.1°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 ± 0.04°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, 19th edition, method 1995.