# Plymouth Ponds and Lakes Stewardship (PALS) Project Monitoring Program

**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 2014-2016

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Coastal Systems Program, SMAST/UMassD and
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## 1. Distribution List

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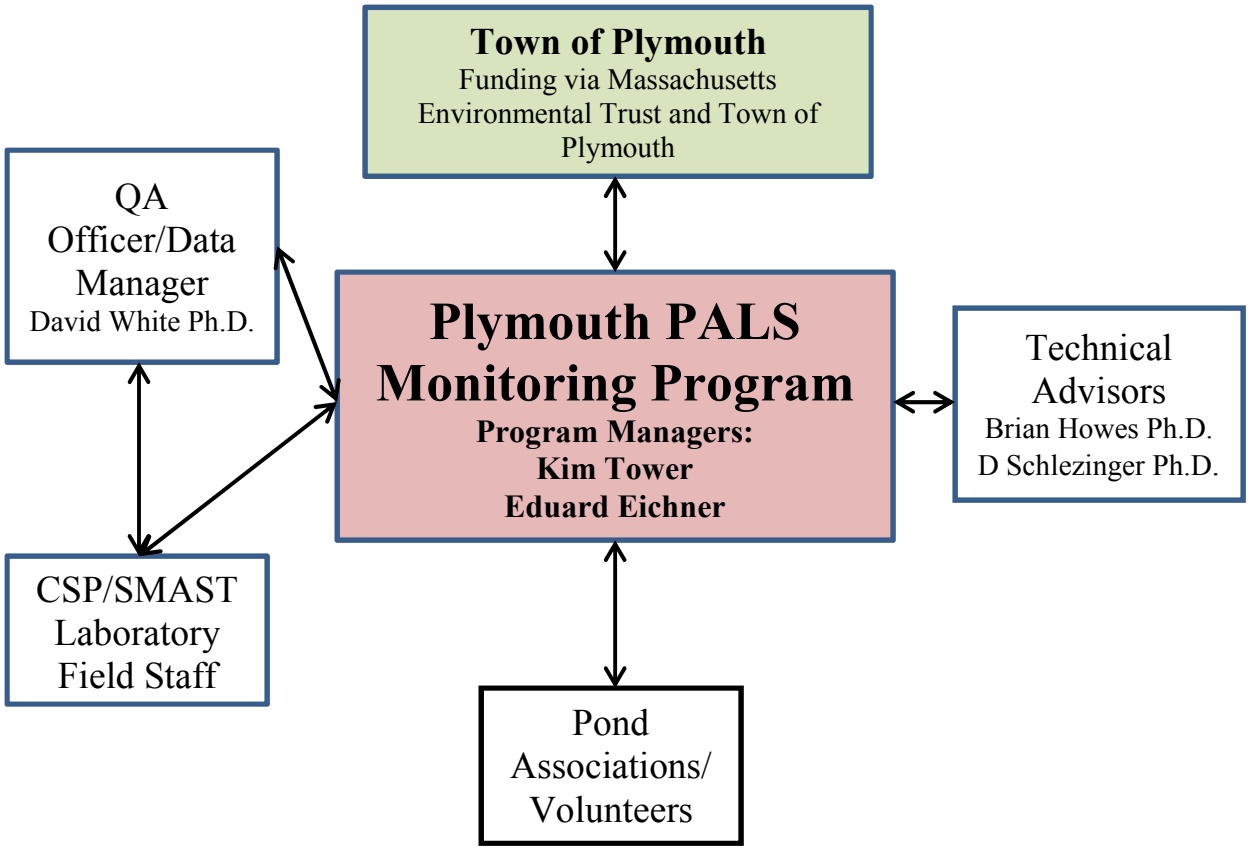
**2. Program Organizational Chart**



## 2.1 Project Partners and Responsibilities

| Title | Responsibilities |
|---|---|
| Project Manager 1 | Manage finances, coordinate with pond associations, and file necessary updates with funding source.<br>Project Manager1: Kim Tower |
| Project Manager 2 | Develop project scope, coordinate sampling and training of volunteers, sampling locations, field data collection, laboratory reporting, review data and sampling accuracy, analysis integrity, data review<br>Project Manager2: Eduard Eichner |
| Technical Advisors | Assist with development of program objectives, data quality objectives, and methods, facilitate implementation of action plans when possible, use data and case studies to inform state water policies where appropriate. Assist with data analysis.<br>Brian Howes, David Schlezinger and P.M. 2, Eduard Eichner |
| Field Staff/Volunteers | Volunteers will be trained with sampling procedures and will conduct sampling of multiple ponds. Remaining ponds 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. Handle and analyze samples using standard methods and performs all quality control checks as required by their QAPP. Provide results of analysis in a timely fashion. Work with Project Manager, and others as appropriate, to resolve any issue that may arise during the sampling season.<br>Brian Howes, Director; Sara Sampieri Horvet, Facility Manager |
| Data Manager | Data from the Lab and field data are collated by Data Manager/ProjectManager-2. Data is maintained by Data Manager/ProjectManager-2 and shared with Project Manager-1. Project Manager-1 will make the data public via the town website.<br>Data Manager-1: Kim Tower; Data Manager-2: Eduard Eichner |
| Quality Assurance Officer | Verify that data quality objectives have been met. Assist with quality control questions or issues that arise during monitoring season. Review reporting of water quality results. |

## 3. 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 regards to eutrophication of various water bodies. Town has recently received Massachusetts Environmental Trust (MET) funding 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.

The Plymouth PALS program will include a snapshot monitoring program that will be designed to provide initial and long-term data about the status of selected ponds. The MET funding will be sufficient to sample 35 ponds. This sampling will occur during August/September in order to gauge what are likely to be worst water quality conditions in the selected ponds. This strategy is the same approach that has been used for the Cape Cod PALS snapshots for the past 13 years. Once snapshot data has been gathered, reporting and public feedback will focus on the production of a Plymouth Pond and Lake Atlas. The Atlas will include 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. It is anticipated that these efforts will be the initial year of an on-going effort that will include regular public feedback and updates.

One of the primary goals of the Plymouth PALS program is to engage and educate the community. This project will include several watershed associations as well as smaller homeowner associations and areas where associations have not been developed. Throughout the project the Town will be communicating with the residents either via mailing or through an association regarding the collection of data, development of the Atlas as well as information on the public meeting. We anticipate an increase in community involvement and education from the Plymouth PALS Project.

## 4. 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. 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 of Plymouth frequently receives inquiries from the residents of Plymouth regarding 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 regards to eutrophication of various water bodies and it would be of extreme value to have prior data and new data reviewed and organized in a Town of Plymouth Pond and Lake Atlas to give a scorecard evaluation format for each of these ponds which would be easy for the layperson to understand.

Several of the waterbodies to be monitored are listed as impaired in the MassDEP Integrated List, but the majority has not been adequately characterized. Establishing a consistent monitoring program based on past monitoring that includes a regular review and reassessment will provide the Town of Plymouth with a consistent and reliable basis for management of pond and lake water quality. 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 thirteen (13) 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 will provide logistical, educational and data synthesis center for water quality monitoring throughout this study. 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. Volunteers 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 volunteers will be trained to follow PALS Snapshot sampling protocols.

| 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<br>Eberhard Von Goeler<br>e.vonGoeler@neu.edu | Collect water samples<br>Public outreach | 5 |
| Billington Sea Association | www.billingtonseapond.com<br>Mike Leary<br>mleary_154@comcast.net | Collect water samples<br>Public outreach | 10+ |
| Six Ponds Association | www.sixponds.org<br>Ed Russell<br>edrussel@aol.com | Collect water samples<br>Public outreach | 30+ |
| Sands of Whitehorse Beach Association | Christine Bostek<br>sandswhitehorsebeachassociation@verizon.net | Access<br>Public outreach | 5+ |
| Friends of Ellisville Marsh | http://ellisvillemarsh.org/<br>Eric Cody<br>eric@ellisvillemarsh.org | Collect water samples<br>Public outreach | 15+ |

**5. Ponds to be sampled**

In this section, we provide a listing of the initial list of ponds to be sampled, their area, their maximum depth, and source of bathymetric information. During the initial 2014 PALS Snapshot, sufficient volunteers have been recruited to sample most ponds; depending on future funding, subsequent years may include Town and/or SMAST staff and expansion of the list of sampled ponds. At the time of writing access is still being negotiated for some of the selected ponds; it anticipated that access to all ponds will be secured before the sampling date. Initial selection of the ponds was based on the Town's internal priority ranking. All ponds are Great Ponds.

| Pond Name | Area (ac) | Max Depth (m) | Samplers | bathymetry |
|---|---|---|---|---|
| BARTLETT | 31 | 1.8 | Volunteer s | Baseline Survey 1970 |
| BIG SANDY | 148 | 11.3 | TOWN/Volunteers | Baseline Survey 1970, DMF |
| BIG WEST | 44 | 4.9 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| BILLINGTON SEA | 279 | 3.4 | TOWN/Billington Sea Association | Baseline Survey 1970, DMF |
| BLOODY | 98 | 11.6 | Six Ponds Association | Baseline Survey 1970, DMF |
| BOOT | 74 | 11.0 | Boot Pond Association | Baseline Survey 1970 |
| CLEAR | 14 | 6.1 | TOWN/Volunteers | Baseline Survey 1970 |
| DEER | 11 | 4.6 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| EZEKIEL'S | 42 | 5.8 | TOWN/Volunteers | Baseline Survey 1970, DMF |
| FORGE | 18 | 3.4 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| FRESH | 67 | 9.1 | TOWN/Volunteers | Baseline Survey 1970, DMF |
| GALLOWS | 51 | 10.0 | Six Ponds Association | Baseline Survey 1970 |
| GREAT HERRING | 419 | 14.0 | Herring Ponds Watershed Association | Baseline Survey 1970, DMF |
| GREAT SOUTH | 290 | 15.5 | Volunteers | Baseline Survey 1970 |
| GUNNERS EXCHANGE | 30 | 7.6 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| HALFWAY | 229 | 4.0 | Six Ponds Association | Baseline Survey 1970, DMF |
| HEDGES | 30 | 2.1 | Volunteers | Baseline Survey 1970 |
| HOYT | 22 | 5.5 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| LITTLE HERRING | 81 | 1.8 | Herring Ponds Watershed Association | Baseline Survey 1970, DMF |
| LITTLE ISLAND (Long Island) | 37 | 5.2 | TOWN | Baseline Survey 1970 |
| LITTLE LONG | 50 | 2.4 | Six Ponds Association | Baseline Survey 1970 |
| LITTLE SOUTH | 66 | 7.0 | SMAST | Baseline Survey 1970 |
| LITTLE WEST | 28 | 4.9 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| LONG | 224 | 31.1 | Six Ponds Association | Baseline Survey 1970, DMF |

| | | | | |
|---|---|---|---|---|
| MICAJAHS | 25 | 7.9 | Volunteer | Baseline Survey 1970 |
| MOREY'S | 26 | 4.0 | TOWN/Volunteers | Baseline Survey 1970 |
| NORTH TRIANGLE | 26 | 3.7 | TOWN/Volunteers | Baseline Survey 1970 |
| ROUND | 22 | 7.3 | Six Ponds Association | Baseline Survey 1970 |
| RUSSELL MILL | 48 | 5.8 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| SAVERY | 30 | 3.7 | Friends of Ellisville Marsh | Baseline Survey 1970 |
| SHALLOW | 21 | 2.1 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| SHIP | 14 | 1.8 | Southeastern Massachusetts Pine Barrens Alliance | Baseline Survey 1970 |
| WALL | 13 | 4.9 | TOWN/Volunteers | Baseline Survey 1970 |
| WHITE ISLAND | 291 | 4.6 | Town/White Island Pond Conservation Alliance | SMAST/CCCGA, 2012 |

## 6. Program Description and Goals

Plymouth DMEA and the Conservation Commission continually refer to the 1970's-era pond reports to answer public and decision-maker questions about water quality management and status. The Plymouth Pond and Lakes Stewards (PALS) program goals are to establish a consistent basis/strategy to collect 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 will begin by gathering water quality data on 35 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 MET funding. The Atlas will be 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 is also partnering with CSP/SMAST to help complete the Atlas, pond sampling and laboratory analysis.

### 6.1 Water Quality Monitoring Protocols for the Ponds

As currently planned, volunteer partners will collect samples from the majority of ponds, while Town of Plymouth staff and CSP/SMAST field staff 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 9 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 (<1 m total depth), two 0.5 m samples are collected. In moderately shallow ponds (≤8 m total depth), at least two water samples are collected, one at 0.5 m and another 1 m off the bottom. If the pond is > 8 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[1] and the consistency of this

[1] 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

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.

### 6.3 Volunteer Monitoring

The majority of the 35 ponds sampled during the initial round of the Plymouth PALS project will be 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 sampling techniques. Town staff may accompany select volunteers to ensure consistency with sampling protocols. Town and CSP/SMAST staff will coordinate one training workshop prior to the first PALS Snapshot sampling. The training workshop will review equipment operation and Plymouth PALS sampling protocols with all volunteers. The workshop will also review chain-of-custody procedures to ensure that volunteers understand proper handling and transfer of collected samples to town personnel for transfer to the CSP/SMAST Analytical Facility.

### 6.4 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 be communicating with the residents either via mailing or through an association regarding the collection of data, development of the Pond Atlas as well as information on the public presentation of the Atlas, its posting on the town website, and future plans for Atlas updates and continued monitoring.

### 6.5 Schedules

***Time Schedule of Plymouth PALS Program***

| TASK | DESCRIPTION | TIMELINE |
|---|---|---|
| 1 | Pond and Lake Database | Completed in Oct 2014 |
| 2 | QAPP | As soon as possible |
| 3 | Sampling and Lab Analysis | Sampling: August 15 through September 30<br>Lab Analysis: October 1 through Jan 30 |
| 4 | Plymouth Pond and Lake Atlas and Presentation | May/June 2015 |

## 7. Water Quality Test Parameters

All the water samples 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

Field parameters/data collection

1) Temperature and Dissolved Oxygen profiles (reading each m to within 1 m of bottom)
2) Secchi disk reading
3) Total station depth
4) Field observations (see PALS Datasheet, Appendix D)

CSP/SMAST Analytical Facility Laboratory is accepted[2] for the parameters listed in this QAPP via the SMAST Coastal Systems Analytical Facility Laboratory Quality Assurance Plan (2003), which included both fresh and salt water nutrient analysis. Water samples are collected and maintained as outlined in Section 8, and 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). The analysis results are submitted to Program Manager-2 for review and comparison with previous results. Analysis results are submitted to the Town with the Plymouth Pond Atlas summarizing the results. 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 Program will employ and satisfy the quality control measures and data quality objectives outlined in this section. The data collected as part of the project is 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 sampling sites are selected to be representative of "average" worst case conditions for the water body or pollution source.

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

[2] the facility has run blind samples from DEP, and has been reviewed by USGS for inorganic N species and gone through laboratory intercalibration on the estuarine inorganic N assays for the Town of Chatham; the laboratory was accepted for the Merrimack River TMDL assays, Department of Defense Ashumet Pond Assays and for the regulatory, Massachusetts Estuaries Project (fresh and salt water nutrients), Alkalinity for CC PALS. Data has been published in over 50 peer reviewed journal articles and 100+ technical reports for various agencies, including MassDEP, etc.

## 8.2 Precision and Accuracy

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 samples are the filling of two 1L bottles from the same collection samplers.

8.2.3. 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.

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

## 8.3 Comparability of Project Data

Cape Cod ponds and lakes are within the same EPA Ecoregion as those in Plymouth and the Cape Cod ponds have been sampled using the same procedures and laboratory, as well as during the sampling period for 13 years through the Cape Cod PALS Program. These data are available to be compared to the 2014 Plymouth data and any future data sets. Since the lab methods are based on the EPA Standard Methods, they should be comparable to state and national results as well. For more information about the pertinent SOPs and laboratory Quality Assuranc reference material, see Appendices E and F.

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 Laboratory. The Laboratory address is:

Coastal Systems Program
Attn: Sara Sampieri Horvet, 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. Water Quality Program, field parameters measured & data objectives | | | | | |
|---|---|---|---|---|---|
| **Parameter** | **Method/ Range Units** | **Sensitivity** | **Precision** | **Accuracy** | **Calibration** |
| Temperature | YSI Dissolved Oxygen Meter/-5 to 45°C | 0.1°C | 0.1°C | 0.3°C | Calibrated in lab before field use by certified thermometer over temperature range |
| Dissolved Oxygen/Hach OX2P (ppm) | YSI Dissolved Oxygen Meter/0 to 20 mg/L | 0.01 ppm | 0.01 ppm | 0.3 ppm | Calibrated in lab before field use by Winkler titration over DO range |
| Water Clarity | Secchi Disk disappearance/ meters | 1 cm | 10 cm | NA | NA: line is measuring tape |

| Table 2. CSP/SMAST Analyte Details for Plymouth PALS Ponds Monitoring Program | | | | | |
|---|---|---|---|---|---|
| **Analyte** | **units** | **Reporting Limit** | **Accuracy/Precision** | **Analysis Method/Type** | **Max Holding Time** |
| Alkalinity | mg/l as CaCO3 | 0.5 | 80-120% Std. Value | Acid Titration [1] | 6 hrs |
| Chlorophyll *a*/ Phaeophytin *a* | µg/l | 0.1 | 80-120% Std. Value | Acetone extraction [2] | 24 hrs |
| Nitrogen, Total | µM | 0.1 | 80-120% Std. Value | Persulfate digestion [3] | Frozen 60 days[6] |
| pH | stnd units | NA | ±0.2 of QC standard | Electrode [4] | 6 hrs |
| Phosphorus, Total | µM | 0.1 | 80-120% Std. Value | Persulfate digestion [5] | Preserved 28 days |

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 (2003)
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.

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 (molybdate/ascorbic acid method).
6) Avanzino, R. J., and V. C. Kennedy (1993), Long-term frozen storage of stream water samples for dissolved orthophosphate, nitrate plus nitrite, and ammonia analysis, Water Resour. Res., 29(10), 3357–3362, doi:10.1029/93WR01684

## 9. Sampling Procedures

The sampling process begins 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 sampling location is determined by review of available bathymetric map and measurement of water depth from acoustic depth sounder or Secchi disk. If GPS coordinates are available, these are used to find the sampling location and site 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).

A Secchi clarity reading is then 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. Viewscopes will not be used. 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.

Water samples are then collected at depths based on the total depth. If the pond is very shallow (<1 m total depth), two 0.5 m samples are collected. At ponds ≤8 m deep, one sample is collected at depths of 0.5 m and 1 m off the bottom. If the pond is >8 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 >11 m deep, one additional sample is collected at 9 m, so a total of four samples are collected at the pond at depths of 0.5 m, 3 m, 9 m, and 1 m off the bottom. A minimum of two samples is collected from each pond. Samples are collected via a 2.2 L Niskin Sampler designed to collect discrete samples at specified depth. Visual inspection of deep water sample is conducted to ensure that no obvious sediment is included; if sediment is found, sample is discarded, device is rinsed 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 laboratory, 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 are 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 Volunteers

Prior to the start of the sampling period (August 15), CSP/SMAST and Town personnel will conduct a training seminar for all involved sampling personnel and volunteers. The seminar will stress consistency of sampling techniques and will review sampling protocols, equipment use, sampling handling procedures, sampling safety, and provide suggested pre-sampling checklists. The seminar will also briefly discuss rationale and potential future uses of collected data.

## 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 laboratory 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, including common-sense boating safety. 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 primary water sampling test results are compiled in Excel spreadsheets, which are submitted to the Town and maintained at CSP/SMAST. MassDEP will be notified when the Plymouth Pond Atlas is posted on the Town website; data (both results and QC data) will be available upon request. CSP/SMAST maintains documentation and records related to the sampling aspects of this program, while Town maintains records of all community outreach and coordination. Electronic records including spreadsheets, digital photographs, notes, and reports are maintained by collectively by CSP/SMAST and the Town.

**Appendix A – Plymouth Pond and Lakes Stewardship 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) Program 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
- 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 and strive to randomize duplicate sampling 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.
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.
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. With little to no air space. 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 monitoring/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) |
|---|---|---|---|---|---|---|---|---|
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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 – CSP/SMAST Analytical Facility SOPs for Plymouth PALS (excerpted from CSP/SMAST Analytical Facility Laboratory Quality Assurance Plan)**

# COASTAL SYSTEMS PROGRAM
# Analytical Facility
# Laboratory Quality Assurance Plan

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*Coastal Systems Laboratory*

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*Lab 114, SMAST 706 South Rodney French Boulevard,*
*New Bedford, MA 02744-1221*
(508)910-6316

# Coastal Systems Analytical Facility
## Summary of Laboratory Quality Assurance Plan

**Revised January 15, 2014**

# 2. Coastal Systems Analytical Facility

# Laboratory Quality Assurance Quality Control

## Excerpted from Laboratory Standard Operating Procedures

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# Water Column and Pore Water Analytes

# 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.

**<u>Data Calculations</u>**

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.

**<u>Interferences</u>**

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.

## 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 $\mu$ filter.
2. In a labeled 16x125 mm test tube add 10 ml sample.

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

**Data Calculations**

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

## Quality Assurance/Quality Control

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

   Standard Additions:
   Add 50 uL of a 1 mM $PO_4$ 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 $\mu$ membrane filters
Turner Designs 10-AU Fluorometer
1 pair filter forceps
250 ml graduated cylinder (6)
250 ml wash bottle

**Consumable Supplies:**
47 mm Nucleopore membrane filters
1 dram vials
Kimwipe tissues
Pasteur Pipettes
Magnesium Carbonate $MgCO_3$ (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 $\mu$ membrane filters can cause interference with the fluorometer. The sample is allowed to settle in the extraction tube before it is pipetted into the cuvette.

## Quality Assurance/Quality Control

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

# 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 tritratable bases. Alkalinity is significant in many uses and treatments of nautral 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.

Total alkalinity (mg $CaCO_3$/L)

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. and will continue adding titrant until the sample is reduced exactly 0.30pH units. Record the volume titrated (mL)

**Calculation:**

Alkalinity (mg $CaCO_3$/L)

= (2B –C) x 50000 x 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.

## Appendix F – CSP/SMAST Analytical Facility – 2014 QA Summary Results

**2014 QA SUMMARY SHEET**

| | Mean | CV | STD | MIN | MAX | Range | n |
|---|---|---|---|---|---|---|---|
| PO4 5uM Standards | 5.00 | 0.02 | 0.12 | 4.76 | 5.25 | 0.49 | 22 |
| NH4 10uM standard | 9.99 | 0.05 | 0.52 | 9.35 | 11.11 | 1.76 | 17 |
| TN 25uM Standard | 26.12 | 0.03 | 0.68 | 24.33 | 27.04 | 2.71 | 31 |
| pH 7 Standard | 7.00 | 0.01 | 0.05 | 6.84 | 7.14 | 0.30 | 93 |
| 32ppt Salinity standard | 32.70 | 0.01 | 0.17 | 32.20 | 32.90 | 0.70 | 21 |
| 50,000mS Conductivity standard | 50.24 | 0.01 | 0.26 | 49.80 | 50.70 | 0.90 | 21 |
| CHLA 200ug/L standard | 190.33 | 0.02 | 3.51 | 187.00 | 194.00 | 7.00 | 3 |
| CHLA 100ug/L standard | 91.67 | 0.03 | 2.63 | 90.10 | 94.70 | 4.60 | 3 |

| | Mean(uM) | CV | STD | MIN | MAX | Range | n |
|---|---|---|---|---|---|---|---|
| TN blank | 1.77 | 0.26 | 0.46 | 1.04 | 3.34 | 2.30 | 31 |
| PO4 Blank | 0.04 | 1.40 | 0.05 | 0.00 | 0.15 | 0.15 | 25 |
| NH4 Blank | 0.34 | 0.92 | 0.32 | 0.00 | 1.45 | 1.45 | 21 |

| | % recovery | n |
|---|---|---|
| TN STD ADDS | 102% | 8 |
| TP STD ADDS | 113% | 14 |

| | % Difference | n |
|---|---|---|
| TN REPS (lachat dups) | 0.25% | 10 |

| | % Difference | n |
|---|---|---|
| TN LAB DUPS | 3.31% | 9 |
| TP LAB DUPS | 8.25% | 25 |
| pH LAB DUPS | 0.98% | 61 |
| ALK LAB DUPS | 9.64% | 61 |

| | % Difference | n |
|---|---|---|
| CHLA FIELD DUP | 14.20% | 92 |
| pH FIELD DUP | 0.81% | 57 |
| ALK FIELD DUP | 5.74% | 57 |