

# Quality Assurance Project Plan

## Blue Hill Bay Coastal Monitoring Program

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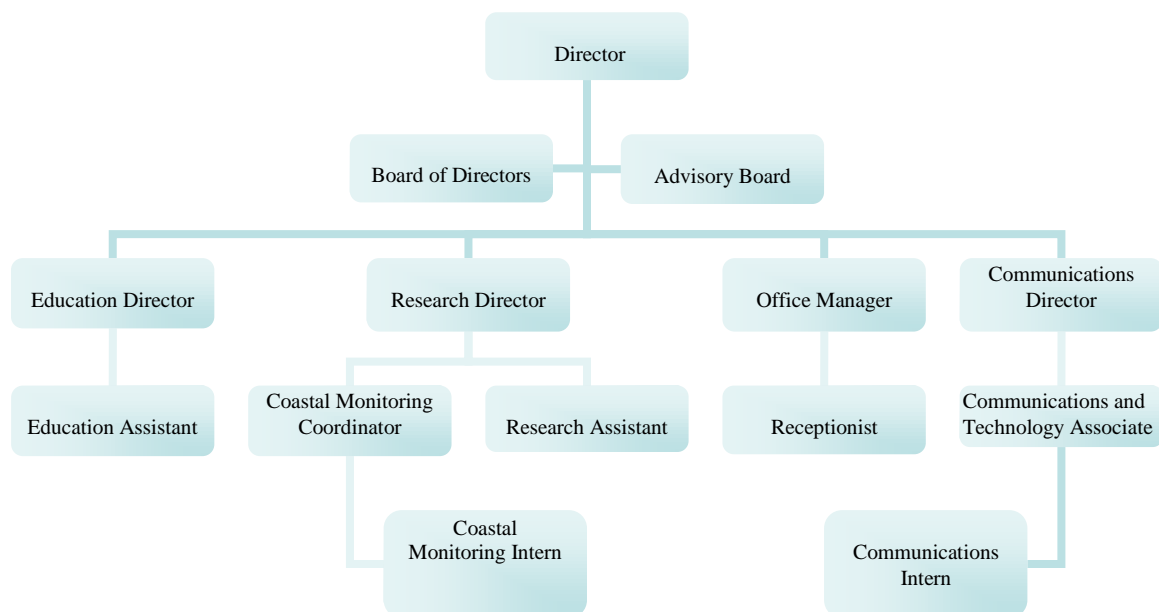
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## 1.4 PROJECT ORGANIZATION

The Marine Environmental Research Institute (MERI) is a 501(C)3 nonprofit charitable organization dedicated to scientific research and education on the impacts of pollution on marine life and human health. Through multidisciplinary research, research dissemination, education, and public outreach, the organization strives to protect the health and biodiversity of the marine environment for future generations.

The organizational structure of MERI for the development and implementation of the Blue Hill Bay Coastal Monitoring Program is outlined in Figure 1-1.

**Figure 1-1 Organizational Structure at Marine Environmental Research Institute**



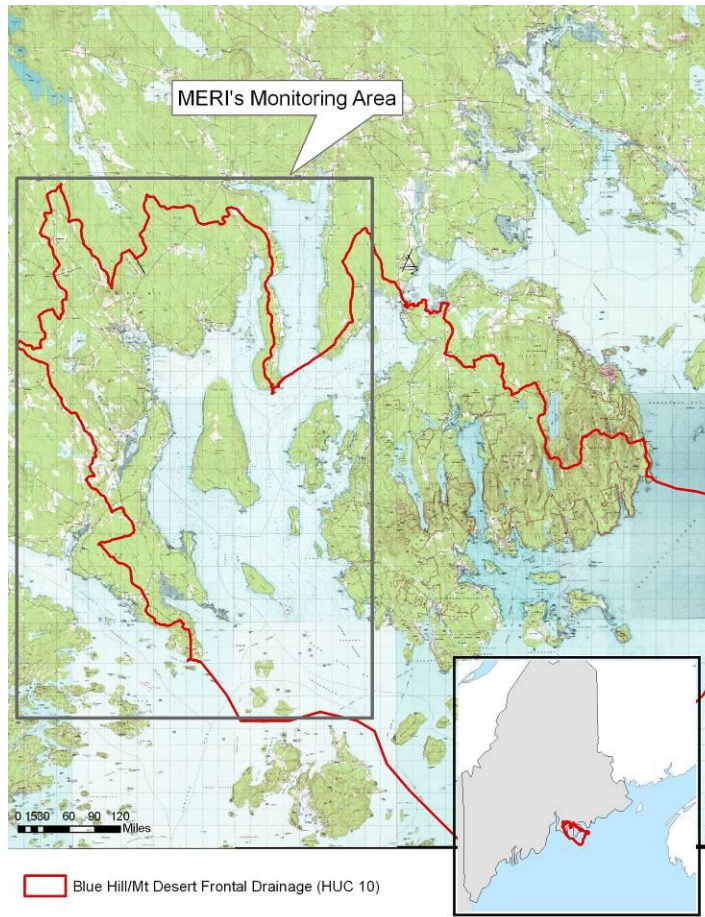
## 1.5 BLUE HILL BAY WATERSHED DEFINITION AND BACKGROUND

The Blue Hill Bay Coastal watershed (technically named the Blue Hill/Mount Desert Frontal drainage) is a 260,632 acre watershed located in coastal Hancock County, Maine. Of the 260,632 acres, only 106,979 are terrestrial, the remaining acreage is predominantly coastal waters. This HUC 10 watershed encompasses 13 towns and has 287.12 miles of shoreline. It is fed by the Union River Bay and Lower Penobscot watersheds and is bordered by Bagaduce, Stonington and the Frenchman Bay watersheds. As a coastal watershed, it is the interface between land and sea, and therefore is the best place to monitor the terrestrial inputs to Blue Hill Bay.

Home to marine mammals, shorebirds, and a network of conservation lands, Blue Hill has the highest acreage of diverse habitat types in the larger watershed according to the Maine Natural Areas Program. Blue Hill Bay is one of the primary seal pupping areas on

the East Coast and, in 2001, there were approximately 13,000 harbor seals and 600 grey seals in the area during the pupping season. A 2008 habitat survey found the area to contain 43,000 acres of shellfish beds, 23 eagle nests, 1,604 acres of shorebird nesting habitat, 27 major seal haul-outs and 480 acres of eelgrass beds.

The watershed is characterized by multiple land uses including the commercial center of Ellsworth, residential areas, open pasture and row crop agriculture as well as protected acreage (Acadia National Park and local conservation areas). There are also multiple municipal waste-water treatment plants and landfills, unmonitored residential septic systems, grand-fathered overboard discharges, marinas, boatyards and abandoned mine sites within the boundaries of the watershed.



**Figure 2:** The Blue Hill Bay/ Mt. Desert Frontal Drainage is a 106,979 acre watershed encompassing 13 towns (outlined in red). The smaller areas outlined within show the sub-watersheds. The inset shows how the Blue Hill Watershed is nested within the larger Maine Coastal Watersheds. The watershed boundaries were updated in 2009 to reflect the new hydrologic units set by the USGS. MERI monitors sites in the western part of the bay (within the gray rectangle).

As population growth and development pressure continues to strain the resources in the area, it has become apparent that there is a fundamental lack of knowledge of the health and capacity of the watershed. This project was created in order to generate baseline data for these previously unstudied areas in the hopes that it will be used as a reference for future monitoring and development in the region. The data gathered will be used to verify water quality standards (Appendix 1), identify sources of pollution and increase awareness of sustainable watershed management. This study was initiated with the help of the Maine Department of Environmental Protection, Maine Department of Marine Resources, Blue Hill Heritage Trust, Friends of Blue Hill Bay and community volunteers to establish a long-term scientific assessment of water quality in and around Blue Hill Bay.

Data from the project will be compiled into annual reports that will be available to the general public as well as on the MERI website ([www.meriresearch.org](http://www.meriresearch.org)). A summary of program progress and findings will also be shared annually with the Town of Blue Hill at an open meeting following each field season. Data will also be available for review by state and municipal agencies as well as neighboring conservation groups. In addition, MERI's education division regularly shares results with local schools and involves students in coastal monitoring projects.

## **1.6 BLUE HILL BAY COASTAL MONITORING PROGRAM**

The Blue Hill Bay Coastal Monitoring Program is a seasonal (April through October) monitoring effort focused on the southern extent of the watershed around the town of Blue Hill, Maine. During the pilot year of 2004, 12 sites were monitored on a weekly basis and three offshore sites were monitored biweekly, (see Appendix 2). In 2005, this was increased to 14 weekly sites and three biweekly sites. By 2011, the sites been expanded to 26 weekly sites and 12 monthly sites plus 6 sites which are sampled opportunistically. Sites were selected to provide a representative sample of watershed conditions, include various land-use types and monitor potential point sources of pollution. MERI plans to expand the geographic scope of the project by adding more sites in future field seasons as funding and staffing allow.

**Table 1-1 Monitoring Project Task Schedule**

	<b>J</b>	<b>F</b>	<b>M</b>	<b>A</b>	<b>M</b>	<b>J</b>	<b>J</b>	<b>A</b>	<b>S</b>	<b>O</b>	<b>N</b>	<b>D</b>
Intern Training				X	X							
Sample Collection				X	X	X	X	X	X	X		
Lab Analysis				X	X	X	X	X	X	X		
Data Analysis	X	X				X	X	X	X	X	X	X
Data Reporting	X	X	X	X							X	X
Planning and Logistics	X	X	X	X								X





**Figure 1-3 Blue Hill Bay Coastal Program Monitoring Sites**

Sampling includes *in situ* measurements and grab sample collection for laboratory analysis.

**Table 1-2 Sampling Parameters**

In Situ	Laboratory Analysis
Temperature	Nitrate
Dissolved Oxygen	Phosphate
Conductivity	<i>Enterococcus</i>
Salinity	
pH	
Turbidity	
Chlorophyll $\alpha$	
Weather Conditions	
Tide Phase	
Depth	

## 1.7 QUALITY OBJECTIVES

Reports generated from this program will be used by government agencies, private organizations and local residents to plan and manage the complex resources of the Blue Hill Bay Coastal Watershed. To achieve this goal, the data produced in this study must be of the highest quality and consistency.

### 1.7a PRECISION

Pre 2010, *in situ* parameters are measured at each site using a *HydroLab DataSonde*® 4a (Hydrolab, Loveland, Colorado, USA) equipped with a *HydroLab Surveyor*® (Hydrolab, Loveland, Colorado, USA). The *Surveyor*® is a hand-held interface unit that allows for on site data storage and subsequent transfer to a computer. After 2010, *in situ* parameters are measured at each site using a *YSI DataSonde 6600v2* (YSI, Yellow Springs, Ohio, USA) equipped with a *YSI MDS 650 Datalogger* for digital storage. Data are also recorded by hand.

The multiprobe is submerged at each site and allowed to equilibrate with the environment for 2-3 minutes before values were recorded. All probes on the meter are calibrated by MERI staff members per the manufacturer's instructions. Temperature is also monitored hourly at selected sites with *TidbiT*® (Onset Computer Corporation, Bourne, Massachusetts, USA) temperature loggers over the entire field season and data are downloaded at the end of the season.

Nutrient samples are taken at each site every month in 100 ml plastic, acid-washed bottles. Labeled bottles are submerged and rinsed twice in the water body before the sample is collected. The sample is then placed on ice and transported to the lab where it is refrigerated and analyzed within 24 hours of collection. Nitrate and phosphate tests are



run on a *HACH Spectrophotometer DR4000* (Hach Company, Loveland, Colorado, USA) with exact laboratory procedures detailed in Appendix 3, 4 and 8.

Eleven sites are sampled weekly for bacteria. Beginning in 2006, *Enterococcus* replaced fecal coliforms as our indicator organism for saltwater sites due to its higher survival rate in marine environments. Disposable 120 ml sterile *IDEXX* (IDEXX Laboratories, Inc., Westbrook, Maine, USA) bottles preloaded with sodium thiosulphate are used to neutralize chlorine activity in the water. Bottles are kept on ice and transported to the lab for analysis within six hours of collection following *IDEXX Colilert*<sup>®</sup>, *Colilert 18*<sup>®</sup> or *Enterolert*<sup>®</sup> procedures outlined in Appendix 5.

A replicate sample study is conducted once a year for all parameters tested. Field measurements taken with the *DataSonde*<sup>®</sup> are verified by filling three identical, clean vessels with sample water at both a fresh and a marine site. The water is thoroughly mixed and repeatedly poured between the three containers to assure a homogenous sample. The *DataSonde*<sup>®</sup> is then lowered into each vessel and measurements are recorded following standard operating procedures. These values are used to calculate standard errors for each sensor on the probe and then compared with the manufacturer's literature.

$$\left[ \frac{\text{Highest} - \text{Lowest}}{\text{Lowest}} \right] \times 100 \leq 10\%$$

A similar study is also conducted on laboratory procedures once a year. Samples are collected from a marine and freshwater site following standard operating procedures. These samples are then analyzed for nutrients and bacteria levels; allowing for the calculation of a standard error for collection, handling and analysis technique.

### **1.7b BIAS**

While it is the goal of this program to accurately sample the entire watershed, the geographic range of the study is limited by the time required to travel from the MERI laboratory to the eastern extent of the watershed. Therefore, field sites for this project are concentrated around the western part of Blue Hill Bay. There are nine HUC-12 watersheds within the HUC-10 Blue Hill Bay/Mount Desert Frontal Drainage and MERI samples six of them. It is the goal of MERI that as support for the program grows, an expanded volunteer program and increased funding will allow for a greater number of field sites. Monitoring sites are also limited by public access to water bodies. MERI's prominent role in the local community has encouraged many land owners to allow sampling on private waterfront property; however, a small number of identified areas of concern remain closed to sampling.

In addition to sampling bias, inherent method and reagent bias also exists. Ferric iron, nitrite, extreme pH values and chloride concentrations above 100 mg/L can all interfere

with the nitrate procedure. The phosphorus method is subject to interference by extreme pH and turbidity as well as several metals including aluminum, copper, iron and nickel. Turbidity and pH readings are taken at each site prior to nutrient sample collection, conductance and salinity values are also recorded to determine the prevalence of potentially interfering metals and salts. The *Colilert*<sup>®</sup> and *Colilert 18*<sup>®</sup> procedures can yield false positives for coliforms in the presence of heterotrophic bacteria greater than 2,000,000 colonies per 100 ml and therefore in 2008, their use was discontinued. However, marine *Bacillus spp.* is known to interfere with the *Enterolert*<sup>®</sup> procedure; to account for this interference all saltwater samples will undergo a tenfold dilution per IDEXX recommendations.

### 1.7c REPRESENTATIVENESS and COMPARABILITY

For the purposes of this study, land use types within the Blue Hill Bay Watershed have been divided into water body types (Table 1-3). Multiple monitoring sites were established to represent each classification.

**Table 1-3 Active and Historical Monitoring Sites**

Site Name	Latitude	Longitude	Water Body Type	Status	Sampling Platform
3rd Pond	44.4002500	-68.6217670	Freshwater	Active	Onshore Fresh
4th Pond	44.4080670	-68.6386830	Freshwater	Active	Onshore Fresh
ABC	44.2614597	-68.5290241	Saltwater	Active	Onshore Salt
Bachelders Brook	44.2768540	-68.5548590	Freshwater/Saltwater Interface	Active	Onshore Salt
Bartlett Island	44.3337950	-68.4463690	Saltwater	Active	Offshore
Blue Hill Harbor	44.4060000	-68.5652000	Saltwater	Active	Onshore Salt
Blue Hill Park	44.4099500	-68.5847170	Freshwater/Saltwater Interface	Active	Onshore Salt
Carleton Mid	44.3806670	-68.6140000	Freshwater	Active	Onshore Fresh
Carleton Upper	44.4107330	-68.6424830	Freshwater	Active	Onshore Fresh
Carrying Place	44.4410300	-68.4702840	Saltwater	Active	Onshore Salt
Carter Preserve	44.4559860	-68.4807720	Freshwater/Saltwater Interface	Active	Onshore Salt
Closson Cove	44.3190420	-68.4999440	Saltwater	Active	Offshore
Coop Stream	44.4148500	-68.5834300	Freshwater	Active	Onshore Fresh
Country Club	44.4020500	-68.5742000	Saltwater	Active	Onshore Salt
Country Club Beach	44.4008330	-68.5636700	Saltwater	Active	Onshore Salt
Curtis Cove	44.4159890	-68.5156040	Freshwater/Saltwater Interface	Active	Onshore Salt
Deep Cove	44.3586320	-68.5219190	Saltwater	Active	Offshore
Deep Hole	44.2977150	-68.5079870	Saltwater	Active	Offshore
Eagle Island	44.2128790	-68.4521840	Saltwater	Active	Offshore

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East Blue Hill Ramp	44.4159410	-68.5217360	Saltwater	Active	Onshore Salt
Golf Course	44.4015330	-68.5739300	Freshwater	Active	Onshore Fresh
Great Marsh	44.3269350	-68.5891270	Freshwater/Saltwater Interface	Active	Onshore Salt
Hardwood Island	44.3102800	-68.4457250	Saltwater	Active	Offshore
Inner Salt Pond	44.3547110	-68.5823280	Freshwater/Saltwater Interface	Active	Onshore Salt
KYC Dock	44.4092890	-68.5645800	Saltwater	Active	Onshore Salt
KYC Mooring	44.4054640	-68.5645700	Saltwater	Active	Offshore
Landfill Stream	44.4565800	-68.5296300	Freshwater	Active	Onshore Fresh
Little Peters Brook	44.4142940	-68.5725260	Freshwater	Active	Onshore Fresh
Long Island North	44.3794350	-68.4937490	Saltwater	Active	Offshore
McHeards Cove	44.4176330	-68.5237000	Freshwater/Saltwater Interface	Active	Onshore Salt
McHeards Cove Offshore	44.2276810	-68.5329740	Saltwater	Active	Offshore
McHeards Marsh	44.4659700	-68.5351270	Freshwater	Active	Onshore Fresh
Mill Stream	44.4134500	-68.5871330	Freshwater/Saltwater Interface	Active	Onshore Fresh
Naskeag	44.2291080	-68.5344300	Saltwater	Active	Onshore Salt
Opechee Dock	44.2118374	-68.4860712	Saltwater	Active	Offshore
Peters Brook	44.4157500	-68.5713500	Freshwater	Active	Offshore
Peters Cove	44.4142100	-68.5717100	Freshwater/Saltwater Interface	Active	Onshore Fresh
Pretty Marsh	44.3352600	-68.4094040	Saltwater	Active	Onshore Salt
RT 172 Marsh	44.4659700	-68.5351270	Freshwater	Active	Offshore
Salt Pond	44.3740330	-68.5596670	Saltwater	Active	Onshore Fresh
South Blue Hill Dock	44.3538280	-68.5469690	Saltwater	Active	Onshore Salt
Surry Wharf	44.4937080	-68.5001300	Freshwater/Saltwater Interface	Active	Onshore Salt
Tamworth	44.4453080	-68.6247490	Freshwater	Active	Onshore Salt
Tinker Island	44.2635190	-68.4787500	Saltwater	Active	Onshore Fresh
1st Pond	44.3795663	-68.6084041	Freshwater	Active	Offshore
Bold Water	44.3098300	-68.5649810	Saltwater	Inactive	Onshore Fresh
Camp Stream	44.4120000	-68.6628300	Freshwater	Inactive	Onshore Salt
Carleton Lower	44.3806670	-68.6140000	Freshwater	Inactive	Onshore Fresh
Hardwood Island South	44.3088760	-68.4467980	Saltwater	Inactive	Onshore Fresh
Jordan River	44.4421760	-68.3568480	Freshwater/Saltwater Interface	Inactive	Offshore
McHeards Stream	44.4212900	-68.5258200	Freshwater	Inactive	Onshore Salt
Mill-Upper	44.4198170	-68.5982830	Freshwater	Inactive	Onshore Fresh

Morgan Bay	44.4292440	-68.4910010	Saltwater	Inactive	Onshore Fresh
North Beach	44.3836000	-68.5031000	Saltwater	Inactive	Onshore Salt
Parker Lane	44.4028990	-68.5645200	Saltwater	Inactive	Offshore
Patten Pond	44.5272390	-68.5175880	Freshwater	Inactive	Onshore Salt
Salt Camp	44.3361670	-68.5315300	Saltwater	Inactive	Onshore Fresh
Seal Cove MDI	44.2815660	-68.4098230	Saltwater	Inactive	Offshore
Union River Bay	44.4823800	-68.4305340	Saltwater	Inactive	Offshore

Before 2011, inland and shore sites were monitored every week during the field season regardless of weather or storm conditions. All estuarine and shore sites were monitored at ebb tide to account for run-off from surrounding upland areas and input from streams. Offshore sites were monitored biweekly at high tide for accessibility reasons. As of 2011, freshwater sites are monitored monthly and offshore and coastal sites are monitored weekly, taking note of the tide. With as many sites as MERI monitors now, we cannot monitor at the ebb tide consequently, tide phase is noted for later analysis of how it affects water quality parameters. All measurements are taken within 1 meter of the water surface except for offshore sites where values are recorded at both 0.5 and at 5.0 meters.

### 1.7d ACCURACY

Until the 2010 field season, MERI used a *HydroLab DataSonde® 4a* multiprobe. Specifications for the applicable parameters are outlined in Table 1-4. In the 2006 field season, MERI replaced the current membrane-type dissolved oxygen probe on the *DataSonde®* with a luminescent dissolved oxygen (LDO) probe.

**Table 1-4 *DataSonde®* and *TidbiT®* Specifications**

Parameter	Range	Accuracy	Resolution
Salinity	0-70ppt	± 0.2ppt	0.01
Turbidity	0-3000 NTU	± 1% up to 100NTU ± 3% from 100-400 ± 5% from 400-3000	0.1 NTU from 0- 400 NTU 1 NTU above 400 NTU
Depth	0-25 m	± 0.05m	0.01m
DO	0-50mg/L	± 0.2mg/L for 20 mg/L or less ± 0.6mg/L for over 20 mg/L	0.01mg/L
Specific Conductance	0-100mS/cm	± 0.001mS/cm	4 digits
pH	0-14	± 0.2	0.01
Chlorophyll <i>a</i>	0-500 ug/L	0.03 ug/L	0.01 ug/L



Nitrate	0-100mg/L-N	± 2mg/L-N	0.01mg/L-N
LDO	0-20mg/L	± 0.1 up to 8 mg/L ± 0.2 above 8 mg/L	0.01 mg/L
Temperature ( <i>DataSonde</i> ®)	-5 to 50 °C	± 0.10 °C	0.01 °C
Temperature ( <i>TidBiT</i> ®)	-4 to 38 °C	± 0.4 °C	0.3 °C

Starting in 2010, MERI uses a *YSI DataSonde 6600v2*® multiprobe. Specifications for the applicable parameters are outlined in Table 1-5.

**Table 1-5 *YSI DataSonde 6600v2*® Specifications**

Parameter	Range	Accuracy	Resolution
Salinity	0 to 70 ppt	0.1 ppt,	0.01 ppt
Turbidity	0 to 1000 NTU	+/- 2% of the reading	0.1 NTU
Depth	0 to 200 m	+/- 0.3 m	0.001 m
Optical DO mg/L	0 to 50 mg/L	0.2 mg/L	0.01 mg/L
Optical DO %	0 to 500 % air saturation	+/- 1 % of the reading	0.1 % air saturation
Conductivity	0 to 100 mS/cm	+/- 0.5% of reading + 0.001 mS/cm	0.001 mS/cm to 0.1 mS/cm
pH	0 to 14 units	+/- 0.2 units	0.01 units
Chlorophyll $\alpha$	0 to 400 µg/L	No specification provided	0.1 µg/L Chl;
Temperature	-5 to 50 °C	+/- 0.15 °C	0.01 °C

Currently, both nitrate and total phosphate are measured from grab samples collected at each monitoring site on a *HACH Spectrophotometer DR4000* (Table 1-6). Instrument blanks are performed for each batch of samples analyzed.

**Table 1-6 Spectrophotometer Specifications**

Parameter	Method	Range	95% Confidence
Nitrate	Cadmium Reduction	0-5.0 mg/L NO <sub>3</sub> -N	± 0.1 mg/L
Phosphate	Ascorbic Acid Method	0-3.59 mg/L PO <sub>4</sub>	± 0.06 mg/L PO <sub>4</sub>

In addition to these accuracy checks, MERI will submit samples from three sites to the Sawyer Environmental Chemistry Research Laboratory in Orono, Maine for analysis once a year. This independent source will verify the accuracy of nitrate and phosphate values. Before 2010, dissolved oxygen, pH and temperature readings were verified on a weekly basis at randomly chosen sites by using a calibrated *HydroLab DataSonde*® 4a.

Values must show less than 10% difference between the project data and the secondary results:

$$\left[ \frac{\text{MERI} - \text{QA}}{\text{QA}} \right] \times 100 \leq 10\%$$

As funding allows, bacterial samples will also be sent out to an independent lab for comparison of results and possible source determination.

## **1.8 SPECIAL TRAINING**

Field and laboratory staff, as well as the Coastal Monitoring Intern, undergo comprehensive training on safety, field instrument use, sample collection, clean lab techniques, spectrophotometer use, *IDEXX*® procedures, autoclave use, waste disposal and Global Positioning Systems (GPS). Standard operating procedures are catalogued in a reference guide and kept on file in the MERI laboratory. A comprehensive manual of training objectives and goals is provided to each intern and employee involved in the Coastal Monitoring program. Training is provided by the Coastal Monitoring Coordinator, following a detailed checklist of requirements (Appendix 6).

All training is completed by the first month of the field season and no new staff members or interns are allowed to collect samples or perform analysis until all aspects of the training program have been fulfilled. Current staff members are required to attend an annual training update session before the beginning of the field season. All training is documented in the training manual and kept on file in the water quality laboratory.

Community involvement and volunteer support are critical to achieving the goals of this program. Volunteers are encouraged to actively participate in the monitoring effort, but due to the technical nature of this project, are always supervised by a trained MERI staff member or intern.

## **1.9 DOCUMENTS and RECORDS**

Pre 2010, all field data collected with the *DataSonde*® was digitally collected on the *Surveyor*® unit and then downloaded onto a laboratory computer. The digital copies were converted into Excel spreadsheets according to sampling event and stored on the hard drive as well as on the MERI computer server on a monthly basis. These data sets were archived into folders for each sampling season and will be kept on file for the duration of the monitoring program.

In addition to the digital copy, a hand-written version of the field data is recorded at the time of sampling along with environmental observations and the names of the sampling

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personnel. An example of this data sheet is given in Appendix 7. These sheets are then entered into the field section of the archive binder in the MERI water quality lab. Data generated from laboratory testing of nutrients and bacterial counts are entered on a separate data sheet on the day of analysis. These sheets are entered into the laboratory section of the same archive binder. An example of this data sheet is given in Appendix 8. The archive binder will be maintained permanently in the MERI water quality lab by the Coastal Monitoring Intern.

Regular progress reports will be presented to the MERI Board of Directors throughout the field season. A final report will be compiled at the conclusion of each monitoring season to summarize findings from the year, identify trends and anomalies with previous data and to propose alterations to the program for future research.

This Quality Assurance Project Plan (QAPP) will be maintained by MERI's Coastal Monitoring Coordinator and will be available in the main office at the MERI center. The document will be reviewed by the Director, Coastal Monitoring Coordinator and the Coastal Monitoring Intern before the beginning of each field season and as changes to the program dictate. Revisions will be circulated among all parties on the distribution list with instructions to disregard all previous versions of the QAPP.

## **DATA GENERATION AND ACQUISITION**

### **2.1 SAMPLING DESIGN and METHODS**

Monitoring sites are chosen to accurately reflect the condition of a portion of the Blue Hill Bay Watershed. Sites are classified by water body type as well as the primary land use in the surrounding area. As this study evolves, MERI strives to sample three distinct sites within each water body/land use category. These classifications range from pristine conservation areas to possible point sources of pollution including the municipal wastewater treatment plant, marinas and overboard discharges.

The latitude and longitude of each monitoring site is recorded with a *Garmin eTrex* (Garmin International, Olathe Kansas, USA) Global Positioning System device. A general description and physical directions are also recorded and included in program reports. These sites are sampled weekly by two MERI staff members. One technician performs *in-situ* measurements with the *DataSonde*® and operates the *Surveyor*® unit, while the other technician records the *DataSonde*® readings and collects the grab sample for nutrient or bacterial analysis.

**Table 2-1 Monitoring Schedule**

<b>Site Type</b>	<b>Analysis</b>	<b>Frequency</b>
Freshwater/Shore	<i>TidbiT</i> ® Temperature	Hourly
Freshwater/Shore	In Situ, <i>DataSonde</i> ®	Weekly
Freshwater/Shore	Bacteria	Biweekly
Freshwater/Shore	Nutrients	Biweekly
Marine Off Shore	In Situ, <i>DataSonde</i> ®	Biweekly
Marine Off Shore	Bacteria	Biweekly

For stream readings, the *DataSonde*® is positioned in a moving section of the main current flow upstream from the technician. For pond and shore sites the technician wades in to a depth of approximately one meter and then lowers the probe, careful not to immerse the *DataSonde*® into the sediment. Offshore sites are monitored from a MERI research vessel by lowering the *DataSonde*® over the up-current side of the boat to a depth of 0.5 and 5.0 meters.

Nutrient grab samples are collected in hydrochloric acid-washed 100 ml plastic bottles. Samples are taken following the EPA Methods Manual for Stream Monitoring; bottles are submerged upside down and slowly turned into the stream flow and brought to the



surface. Bottles are rinsed twice before the actual sample is collected. A complete methods description can be found in Appendix 9. Due to the sodium thiosulphate powder required for the procedure, bacterial grab samples are taken with sterile 120 ml *IDEXX* bottles submerged just below the surface.

*TidbiT*<sup>®</sup> temperature loggers are anchored at selected sites for the entire field season. Location of the loggers is documented upon deployment in the spring but no flagging is made at the site to reduce disturbance by the public. Data is downloaded from the loggers in the field via an optic transfer shuttle at two points during the year.

## **2.2 SAMPLE HANDLING and CUSTODY**

All bottles are labeled with the established site name, date and time of sampling. While in the field, all samples are the responsibility of the two-person team and are kept on ice for the duration of the monitoring day. Once at the lab, bacterial samples are prepared and incubated within six hours of collection. Nutrient samples are placed in the laboratory refrigerator and are analyzed within 24 hours. The Coastal Monitoring Intern assumes responsibility for all samples once they have returned from the field.

## **2.3 ANALYTICAL METHODS**

MERI staff follow established *HACH* standard operating procedures for the analysis of nitrate (cadmium reduction method) and total phosphate. See Appendix 3 and 4 for methods. Bacterial monitoring is performed via *IDEXX* methods as outlined in the *Enterolert* procedures in Appendix 5. Hazardous waste generated from the cadmium reduction of water samples for nitrate analysis is properly stored in labeled containers and transferred to a licensed hazardous waste carrier. All positive bacterial trays are autoclaved prior to disposal.

## 2.4 QUALITY CONTROL

The Blue Hill Bay Coastal Monitoring Program implements a variety of quality control measures.

**Table 2-2 Quality Control Checks**

Parameter	QC Measure	Frequency	Required Result
<i>DataSonde</i> <sup>®</sup> Dissolved Oxygen	Zero Standard	Before each field day	< 0.5 mg/L
Bacteria	Negative Control	Every 20 Samples	No colony growth
<i>HACH</i> Nitrate	DI Blank	Every 20 Samples	Below Detection Limit
<i>HACH</i> Nitrate	Duplicate Sample	Every 20 Samples	See Formula 1
<i>HACH</i> Nitrate	Matrix Spike	Every 20 Samples	See Formula 2
<i>HACH</i> Phosphate	DI Blank	Every 20 Samples	Below Detection Limit
<i>HACH</i> Phosphate	Duplicate Sample	Every 20 Samples	See Formula 1
<i>HACH</i> Phosphate	Matrix Spike	Every 20 Samples	See Formula 2

Formula 1:

$$\text{Formula 2: } \left[ \frac{\text{Higher} - \text{Lower}}{\text{Lower}} \right] \times 100 \leq 10\%$$

$$\left[ \frac{\text{Result} - \text{Standard}}{\text{Standard}} \right] \times 100 \leq 10\%$$

## 2.5 INSTRUMENT TESTING, INSPECTION and MAINTENANCE

The multi-parameter probes are inspected before use by field staff. The dissolved oxygen membrane is inspected for tears, operation of the circulator is verified and all sensors are checked to be clean and cleared of fouling if necessary. The unit is inspected and serviced by the manufacturer on an annual schedule and as needed.

Laboratory water bath and incubator temperatures are checked with a reference thermometer before the field team begins the monitoring day. *Millipore* (Millipore, Billerica, Massachusetts, USA) deionized water filters are changed and maintained based on manufacturer's specifications. The spectrophotometer performs a daily self-diagnostic test and is inspected by the Coastal Monitoring Coordinator prior to analyzing the first batch of samples of the day.

## 2.6 INSTRUMENT CALIBRATION

All probes on the *DataSonde*<sup>®</sup> are calibrated according to the manufacturer's specifications and as dictated by fouling or membrane damage. The schedule for calibration is outlined in Table 2-3. Standards are purchased directly from *HACH* or *YSI* and are disposed of prior to the expiration date. All calibrations are performed by trained MERI staff and are recorded in the equipment section of the water quality laboratory binder for future reference.

**Table 2-3 Calibration Schedule for MERI Equipment**

Parameter	Frequency	Standard or Method Used
Depth	Weekly	Zeroed at Each Site
DO	Weekly	Barometric Pressure, Air
pH	Monthly	4.00, 7.00, 10.00 Buffers
Turbidity	Monthly	40 NTU StablCal
Spec Conductance	Monthly	1.412 mS/cm, 47.6 mS/cm
Chlorophyll <i>a</i>	Annually	Rhodamine Dye

## 2.7 INSPECTION/ACCEPTANCE of CONSUMABLES

The Coastal Monitoring Coordinator at MERI is responsible for the receipt of all consumables required for this monitoring program. All reagents and standards used for calibration of the multi-parameter probes, and for analysis with the spectrophotometer, are ordered through *HACH* or *Fisher Scientific* (Fisher Scientific Company LLC, Indiana, Pennsylvania, USA). Sterile bottles, reagents, comparators and trays required for *Enterolert*<sup>®</sup> procedures are purchased through *IDEXX*. Age and recommended shelf-life for each reagent is noted and all chemicals are disposed of before the expiration date.

## 2.8 NON-DIRECT MEASUREMENTS

The only non-direct measurements used by the Blue Hill Bay Coastal Monitoring program are tide charts provided by [saltwatertides.com](http://saltwatertides.com).

## **2.9 DATA MANAGEMENT**

Weather conditions, tide level, sampling time and observer names are recorded on field data sheets (Appendix 7). This data sheet also documents the values measured on the *DataSonde*® at the time the digital file is logged for each site. Analytical data for nutrient and bacterial monitoring are recorded by the Coastal Monitoring Intern on laboratory data sheets at the completion of each test.

These hard copies are kept on file in the water quality laboratory and entered into a Google Documents spreadsheet on a weekly basis. Field measurements recorded on the *YSI Surveyor* unit are downloaded onto the laboratory computer after each sampling event and copied into a Google document.

MERI has built a customized Access database for the analysis and archival of all data relating to the Blue Hill Bay Coastal Monitoring Program. The Access database will be updated regularly by the Coastal Monitoring Coordinator and Intern. The database will then be archived on the MERI server and used for all future analysis and reports.

## **ASSESSMENT AND OVERSIGHT**

### **3.1 ASSESMENT AND RESPONSE ACTIONS**

All data generation and management procedures are reviewed by MERI's Coastal Monitoring Coordinator on a continual basis. Interns and new staff members are given comprehensive field and analytical training prior to the monitoring season and are directly supervised by experienced technicians during the field season. Existing staff members must undergo an annual update on standard operating procedures at the beginning of each season. The Coastal Monitoring Coordinator is responsible for verifying that all staff members have completed the training program and for spot-checking compliance with accepted protocols throughout the year.

If the Coastal Monitoring Coordinator observes any deviations from the guidelines established in this QAPP that staff member will be required to repeat the training course and will be evaluated by the Coastal Monitoring Coordinator prior to returning to independent sampling work. All field and laboratory procedures involved in this program may be reviewed by representatives from the Maine Department of Environmental Protection or the U.S. Environmental Protection Agency as requested.

### **3.2 REPORTS to MANAGEMENT**

Regular progress reports will be given to MERI's Director and Board of Directors. A complete annual report will be compiled for the Executive Director and Board of Directors to review in February of each year. This report will be available to the public



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on the MERI website at [www.meriresearch.org](http://www.meriresearch.org). As the geographic scope of this program expands, MERI plans to offer presentations and reports to surrounding communities within the Blue Hill Bay Watershed.

## **DATA VALIDATION AND USABILITY**

### **4.1 DATA REVIEW, VERIFICATION and VALIDATION**

The Coastal Monitoring Coordinator and Intern are responsible for the consistency, accuracy and completeness of all field and laboratory data entry. The Coastal Monitoring Coordinator and the Coastal Monitoring Intern maintain records of instrument calibration, service and inspection. All invoices and service records and manuals are kept on electronic file in the MERI water quality laboratory and in a designated folder on the MERI server.

The Coastal Monitoring Coordinator and Coastal Monitoring Intern will collaboratively develop a resolution to any observed faults in instrument calibration and maintenance, sample collection, laboratory analysis or data management. This may include the explanation of an identified quality issue, requesting a repeat analysis or disallowing a dataset.

### **4.2 VERIFICATION and VALIDATION METHODS**

The Coastal Monitoring Intern verifies all sample labels and field data sheets upon return to the MERI laboratory. Any discrepancies are noted on the data sheets and initialed by the technician. Recording errors made on either field or laboratory notes are crossed-out and initialed by the recorder with the correct value entered immediately adjacent to the original value.

Upon completion of the weekly fieldwork, all data are copied and pasted from the *Ecowatch* file downloaded from *YSI DataSonde 6600V2* into Google Documents spreadsheet by the Coastal Monitoring Intern. The Intern then verifies the entries by referencing the original field data. Any outliers or discrepancies are presented to the Coastal Monitoring Coordinator for review. Each year has a separate spreadsheet. There is also a master document where all years are combined. Google Documents allows users to see any changes by user and/or time and also to share data with other users. Any analyses are done by downloading an excel sheet from the online master file.

### **4.3 RECONCILIATION with USER REQUIREMENTS**

Analysis of quality control measures (see Table 2-2) will be made by the Coastal Monitoring Coordinator following each sampling event. Results that fall beyond the required range will be noted on the data sheets for that day and discussed with the Coastal

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Monitoring Coordinator. Appropriate action will be taken prior to the next sampling event based on the nature of the quality control measure including instrument calibration, repeat sampling of a site or evaluation of a standard operating procedure.

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**Appendices**

**5.1 Fresh Water Quality Standards**

Parameter	Organization	Source	Value
Dissolved Oxygen Fresh water	State of Maine	Title 38 - § 464: Classification of Maine Waters	Class A= 7 ppm Class B= 7 ppm Class C= 5 ppm
Turbidity	EPA	Ambient Water Quality Criteria Recommendations, Rivers and Streams in Nutrient Ecoregion VIII	1.3 NTU
Phosphorus	Maine DEP	Comprehensive Surface Water Ambient Water Quality Monitoring and Assessment Strategy, 2005-2015	20 ppb
Nitrate	EPA	National Recommended Water Quality Criteria: Human Health Criteria Table	10 mg/L
Chlorophyll <i>a</i>	Maine DEP	Comprehensive Surface Water Ambient Water Quality Monitoring and Assessment Strategy, 2005-2015	7 ug/L
<i>Enterococcus</i>	Maine Healthy Beaches	<a href="http://www.mainehealthybeaches.org">www.mainehealthybeaches.org</a>	104 Colonies per 100 ml

### 5.2 Historic Site Table

Site Name	Sampling Events: 2004	Sampling Events: 2005	Sampling Events: 2006	Sampling Events: 2007	Sampling Events: 2008	Sampling Events: 2009	Sampling Events: 2010	Sampling Events: 2011
1st Pond	0	0	23	22	20	21	0	0
3rd Pond	25	26	22	22	20	21	22	6
4th Pond	25	26	27	22	19	21	21	6
ABC	0	0	12	12	18	22	25	24
Bachelers Brook	0	0	0	0	0	0	7	18
Bartlett Island	0	0	0	0	0	0	0	20
Blue Hill Harbor	12	0	0	0	0	0	0	0
Blue Hill Park	25	26	23	23	17	24	33	19
Bold Water	0	0	0	0	0	22	0	0
Camp Stream	0	26	0	0	0	0	0	0
Carleton Lower	25	26	25	22	20	21	0	0
Carleton Mid	25	26	26	22	20	21	22	5
Carleton Upper	25	26	26	19	19	21	22	5
Carrying Place	0	0	24	19	20	22	27	26
Carter Preserve	0	0	22	19	20	22	31	24
Closson Cove	0	0	10	0	10	10	16	22
Coop Stream	0	0	21	14	17	21	20	5
Country Club	25	26	24	22	17	22	28	7*
Country Club Beach	0	0	0	22	17	23	32	25
Curtis Cove	0	0	24	19	20	22	31	25
Deep Cove	12	12	11	7	10	13	20	22
Deep Hole	0	0	0	7	0	13	19	22
Eagle Island	0	0	0	0	0	0	4	2
East Blue Hill Ramp	0	0	24	19	20	22	27	0*
Golf Course	0	0	0	22	17	22	24	24
Great Marsh	0	0	26	17	15	21	29	21
Hardwood Island	0	0	20	14	18	14	22	21
Inner Salt Pond	0	0	24	20	19	21	32	25
Jordan River *	0	0	0	0	0	0	1	0
KYC Dock	0	12	23	15	21	22	34	28
KYC Mooring	0	0	0	3	9	17	17	21
Landfill Stream	0	0	19	18	19	21	15	4
Little Peters Brook	0	0	0	6	21	21	23	5
Long Island North	0	0	10	7	8	15	21	21
McHeards Cove	25	26	24	17	19	21	27	10*
McHeards Cove Offshore	0	0	0	0	0	13	22	21
McHeards Marsh	0	0	19	18	20	21	22	5



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McHeards Stream	0	26	0	0	0	0	0	0
Mill Stream	25	26	24	19	14	21	22	5
Mill-Upper	25	26	0	0	0	0	0	0
Morgan Bay	0	0	10	7	9	0	2	0
Naskeag	0	0	0	0	0	23	25	24
North Beach	12	0	0	0	0	0	0	0
Opechee Dock	0	0	0	0	0	0	3	1
Parker Lane	0	0	24	22	17	22	3	0
Patten Pond	0	0	23	19	21	21	0	0
Peters Brook	25	26	23	19	21	21	23	5
Peters Cove	0	0	0	17	19	22	30	24
Pretty Marsh	0	0	0	0	0	0	1	2
RT 172 Marsh	0	0	21	19	20	21	21	5
Salt Camp	0	12	10	7	9	14	21	0
Salt Pond	25	26	25	22	18	22	28	25
Seal Cove MDI	0	0	0	0	0	0	1	0
South Blue Hill Dock	0	0	25	22	18	21	27	24
Surry Wharf	0	0	23	19	20	21	25	24
Tamworth	0	0	22	20	20	21	22	5
Tinker Island	0	0	0	0	0	7	19	14
Union River Bay	0	0	10	1	0	0	0	0

### 5.3 Nitrate Method



## DR/4000 PROCEDURE

## NITRATE

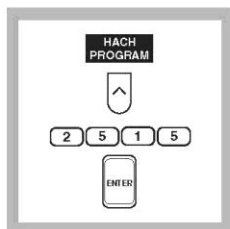
### Method 8192

### Cadmium Reduction Method

### Powder Pillows

### LR (0 to 0.50 mg/L NO<sub>3</sub><sup>-</sup>-N)

**Scope and Application:** For water, wastewater and seawater.  
The estimated detection limit for program number 2515 is 0.01 mg/L NO<sub>3</sub><sup>-</sup>-N.



- 1.** Press the soft key under **HACH PROGRAM**.

Select the stored program number for nitrate, low range, by pressing **2515** with the numeric keys.

Press: **ENTER**

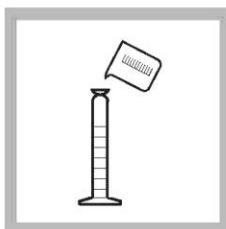
**Note:** If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps. Adjust the pH of preserved samples before analysis.



- 2.** The display will show: **HACH PROGRAM: 2515 N, Nitrate LR**

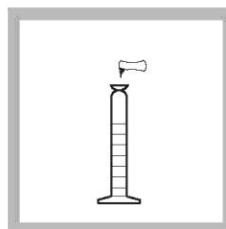
The wavelength (λ), **507 nm**, is automatically selected.

**Note:** A reagent blank must be determined on each new lot of reagent as follows. Prepare a reagent blank by repeating Steps 3 through 14, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under **ZERO**. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under **OPTIONS, (MORE)**, and then **BLANK:OFF**. Enter the reagent blank value and press **ENTER**. Repeat for each new lot of reagent.



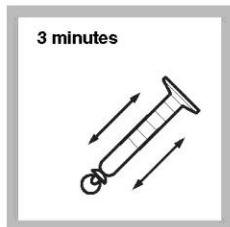
- 3.** Fill a 25-mL graduated mixing cylinder with 15 mL of sample.

**Note:** For proof of accuracy, use a 0.2 mg/L nitrate nitrogen standard solution (see the Accuracy Check section) in place of the sample.

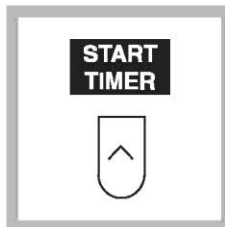


- 4.** Add the contents of one NitraVer 6 Reagent Powder Pillow to the cylinder. Stopper.

## NITRATE, continued



**5.** Press the soft key under **START TIMER**.  
Shake the cylinder vigorously for 3 minutes.



**6.** When the timer beeps, press the soft key under **START TIMER**.  
A 2-minute reaction period will begin.

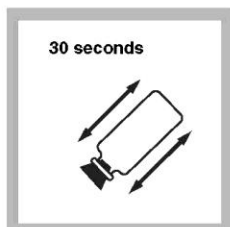
*Note: A deposit of unoxidized metal will remain after the NitraVer 6 dissolves. The deposit will not affect results.*



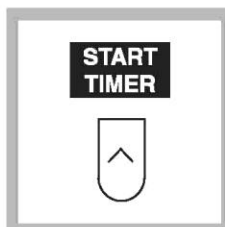
**7.** When the timer beeps, carefully pour 10 mL of the sample into a clean sample cell. Take care not to transfer any cadmium particles.



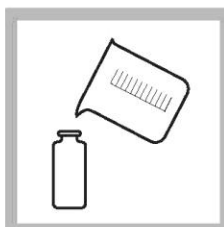
**8.** Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell (the prepared sample). Stopper.



**9.** Press the soft key under **START TIMER**.  
Shake the sample cell gently for 30 seconds.  
*Note: A pink color will develop if nitrate is present.*



**10.** Press the soft key under **START TIMER**.  
A 15-minute reaction period will begin.



**11.** When the timer beeps, fill a second sample cell with 10 mL of original sample (the blank).



**12.** Place the blank into the cell holder and close the light shield.

## NITRATE, continued



**13.** Press the soft key under **ZERO**.

The display will show:

**0.00 mg/L NO<sub>3</sub><sup>-</sup>-N**

**Note:** For alternate concentration units, press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the read screen.

**Note:** If you have entered a reagent blank correction, the display will show the correction.



**14.** Place the prepared sample into the cell holder and close the light shield. The result in mg/L nitrate nitrogen will be displayed.

**Note:** The results can be expressed as mg/L nitrate (NO<sub>3</sub><sup>-</sup>). Press the soft keys under **OPTIONS**, and then **FORM**: to scroll through the available options.

**Note:** Rinse the sample cell and mixing cylinder immediately after use to remove all cadmium particles. Retain the spent sample for proper hazardous waste disposal for cadmium.

## Interferences

**Table 1 Interfering Substances and Suggested Treatments**

Interfering Substance	Interference Level and Treatment
Calcium	100 mg/L
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration.
Ferric iron	All levels
Nitrite	All levels: This method measures both the nitrate and nitrite in the sample. If nitrite is present, the nitrite nitrogen test (Program #2610) should be done on the sample. Pretreat the nitrate nitrogen sample with the following pretreatment. Then subtract the amount of nitrite found from the results of the LR nitrate nitrogen test. <ol style="list-style-type: none"> <li>1. Add 30-g/L Bromine Water dropwise to the sample in Step 3 until a yellow color remains. Mix after each drop.</li> <li>2. Add one drop of 30-g/L Phenol Solution to destroy the color.</li> <li>3. Proceed with the LR Nitrate procedure.</li> </ol>
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels

## **NITRATE, continued**

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### **Sample Collection, Storage and Preservation**

Most reliable results are obtained when samples are analyzed as soon as possible after collection. If prompt analysis is impossible, store samples in clean plastic or glass bottles for up to 48 hours at 4 °C. To preserve samples for longer periods, add 2 mL of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) per liter and store at 4 °C.

Before analysis, warm the sample to room temperature and adjust the pH to 7 with 5.0 N Sodium Hydroxide Standard Solution. Do not use mercury compounds as preservatives. Correct the test result for volume additions by dividing the total volume (acid + base + sample) by the original sample volume and multiplying the test result by this factor.

### **Accuracy Check**

#### **Standard Solution Method**

To test accuracy, use a 0.20-mg/L NO<sub>3</sub><sup>-</sup>-N standard in place of the sample and perform the procedure as described. Prepare this standard by diluting 2.00 mL of a 10-mg/L Nitrate Nitrogen Standard Solution to 100.0 mL with deionized water.

To adjust the calibration curve using the reading obtained with the 0.20-mg/L nitrate nitrogen standard, press the soft keys under **OPTIONS, (MORE)** then **STD: OFF**. Press **ENTER** to accept the default concentration, 0.20-mg/L NO<sub>3</sub><sup>-</sup>-N. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section 1.5.5 *Adjusting the Standard Curve* for more information.

#### **Standard Additions Method**

- a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under **OPTIONS, (MORE)** and then **STD ADD**.
- b. Press **ENTER** to accept the default sample volume (mL), 15. (This is the volume to which standard addition aliquots are added.)
- c. Press **ENTER** to accept the default standard concentration (mg/L), 12.0.
- d. Press the soft key under **ENTRY DONE**.
- e. Fill three 25-mL graduated mixing cylinders with 15 mL of sample.
- f. Snap the neck off a Nitrate Nitrogen PourRite Ampule Standard, 12.0-mg/L NO<sub>3</sub><sup>-</sup>-N.
- g. Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively to the three mixing cylinders. Stopper each and mix thoroughly.
- h. Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under **READ** each time. Each additions reading should reflect approximately 100% recovery.
- i. After completing the sequence, the display will show the extrapolated concentration value and the "best-fit" line through the standard additions data points, accounting for matrix interferences.
- j. See Section 1.4.1 *Standard Additions* for more information.

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**NITRATE, continued**

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**Method Performance**

**Precision**

Standard: 0.30 mg/L  $\text{NO}_3^- - \text{N}_2$

Program	95% Confidence Limits
2515	0.29–0.31 mg/L $\text{NO}_3^- - \text{N}$

For more information on determining precision data and method detection limits, refer to Section 1.5.

**Estimated Detection Limit**

Program	EDL
2515	0.01 mg/L $\text{NO}_3^- - \text{N}$

For more information on derivation and use of Hach's estimated detection limit, see Section 1.5.2. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section 1.5.1.

**Sensitivity**

Program Number: 2515

Portion of Curve:	$\Delta\text{Abs}$	$\Delta\text{Concentration}$
0.004 mg/L $\text{NO}_3^- - \text{N}$	0.010	0.0041 mg/L $\text{NO}_3^- - \text{N}$
0.25 mg/L $\text{NO}_3^- - \text{N}$	0.010	0.0034 mg/L $\text{NO}_3^- - \text{N}$
0.45 mg/L $\text{NO}_3^- - \text{N}$	0.010	0.0027 mg/L $\text{NO}_3^- - \text{N}$

See Section 1.5.3 *Sensitivity Explained* for more information.

**Calibration Standard Preparation**

To perform a nitrate calibration using the Low Range Cadmium Reduction method, prepare calibration standards containing 0.10, 0.30, and 0.50 mg/L  $\text{NO}_3^- - \text{N}$  as follows:

- Into three different 100-mL class A volumetric flasks, pipet 1.00, 3.00, and 5.00 mL of a 10.0-mg/L Nitrate Nitrogen Standard Solution using Class A glassware.
- Dilute to the mark with deionized water. Mix thoroughly.
- Using the Low Range Cadmium Reduction method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

**Summary of Method**

Cadmium metal reduces nitrates in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt couples with chromotropic acid to form a pink-colored product.



## 5.4 PHOSPATE METHOD



### DR/4000 PROCEDURE

### PHOSPHORUS, Reactive (Orthophosphate)

✓ Method 8048

PhosVer 3 (Ascorbic Acid) Method\*

Powder Pillows or AccuVac® Ampuls

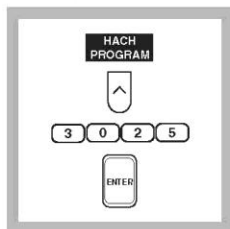
(0 to 2,500 mg/L  $\text{PO}_4^{3-}$ )

**Scope and Application:** For water, wastewater, seawater; USEPA Accepted for reporting for wastewater analyses\*\*. The estimated detection limits for program numbers 3025 and numbered 3030 are 0.045 and 0.031 mg/L  $\text{PO}_4^{3-}$  respectively.

\* Adapted from *Standard Methods for the Examination of Water and Wastewater*

\*\* Procedure is equivalent to USEPA method 365.2 and Standard Method 4500-P-E for wastewater.

### Using Powder Pillows



1. Press the soft key under **HACH PROGRAM**.

Select the stored program number for phosphorus, ascorbic acid method by pressing **3025** with the numeric keys.

Press: **ENTER**

**Note:** If samples cannot be analyzed immediately, see *Sample Collection, Storage and Preservation* following these steps.

**Note:** The Flow Cell and Sipper Modules can be used with this procedure. Use a 25-mL sample and reagents with the Flow Cell Module.



2. The display will show: **HACH PROGRAM: 3025 P React. As. LR**

The wavelength ( $\lambda$ ), **890 nm**, is automatically selected.

**Note:** For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 8, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under **ZERO**. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under **OPTIONS**, (**MORE**), and then **BLANK: OFF**. Enter the reagent blank value and press **ENTER**. Repeat for each new lot of reagent.



3. Fill a sample cell with 10-mL of sample.

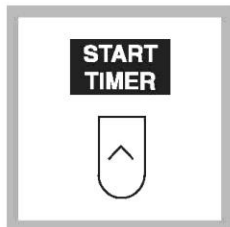
**Note:** For proof of accuracy, use a 1.0 mg/L Phosphate (0.33 mg/L P) Standard Solution listed under **OPTIONAL REAGENTS AND STANDARDS** in place of the sample.



4. Add the contents of one PhosVer 3 phosphate Powder Pillow to the cell (the prepared sample). Swirl immediately to mix.

**Note:** A blue color will form if phosphate is present.

## PHOSPHORUS, Reactive (Orthophosphate), continued



**5.** Press the soft key under **START TIMER**.

A 2-minute reaction period will begin.

**Note:** If the sample has been digested using the Acid Persulfate digestion in this manual, this step requires 10 minutes.



**6.** Fill another sample cell (the blank) with 10 mL of sample. Place it into the cell holder.



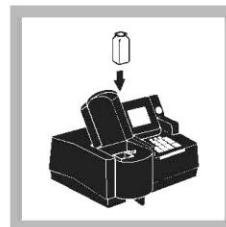
**7.** When the timer beeps press the soft key under **ZERO**.

The display will show:

**0.000 mg/L PO<sub>4</sub><sup>3-</sup>**

**Note:** If you are using a reagent blank correction, the display will show the correction.

**Note:** For alternate concentration units press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the read screen.



**8.** Place the prepared sample into the cell holder. Close the light shield. Results in mg/L PO<sub>4</sub><sup>3-</sup> (or chosen units) will be displayed.

**Note:** The results can be expressed as PO<sub>4</sub><sup>3-</sup>, P or P<sub>2</sub>O<sub>5</sub>. Press the soft keys under **OPTIONS**, and then **FORM**: to scroll through the available options.

### **PHOSPHORUS, Reactive (Orthophosphate), continued**

#### **Interferences**

<b>Interfering Substance</b>	<b>Interference Levels and Treatments</b>
Aluminum	Greater than 200 mg/L
Arsenate	Interferes at any level
Chromium	Greater than 100 mg/L
Copper	Greater than 10 mg/L
Hydrogen Sulfide	Interferes at any level
Iron	Greater than 100 mg/L
Nickel	Greater than 300 mg/L
pH, excess buffering	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment. pH 2–10 is recommended.
Silica	Greater than 50 mg/L
Silicate	Greater than 10 mg/L
Turbidity (large amounts) or color	May cause inconsistent results because the acid in the powder pillow may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles. For highly turbid or colored samples, add the contents of one Phosphate Pretreatment Powder Pillow to 25 mL of sample. Mix well. Use this solution to zero the instrument.
Zinc	Greater than 80 mg/L

Store the PhosVer 3 Phosphate Reagent Powder Pillows and AccuVac Ampuls in a cool, dry environment.

#### **Sample Collection, Storage and Preservation**

Collect sample in plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in phosphate analysis.

Most reliable results are obtained when samples are analyzed as soon as possible after collection. If prompt analysis is impossible, preserve samples up to 24 hours by storing at or below 4 °C.

#### **Accuracy Check**

##### **Standard Additions Method**

- Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under **OPTIONS, (MORE)** and then **STD ADD**.
- Press **ENTER** to accept the default sample volume (mL), 25.
- Press **ENTER** to accept the default standard concentration (mg/L) 50.
- Press the soft key under **ENTRY DONE**.
- Snap the neck off a Phosphate 2-mL Ampule Standard, 50-mg/L  $\text{PO}_4^{3-}$ .
- Use the TenSette Pipet to add 0.1, 0.2 mL and 0.3 mL of standard, respectively to three 25-mL samples and mix each thoroughly (for AccuVac Ampuls, use 50-mL beakers).

## PHOSPHORUS, Reactive (Orthophosphate), continued

- g. Analyze each standard addition sample as described above (use 10-mL aliquots of the standard addition samples for the powder pillow method). Accept the standard additions reading by pressing the soft key under **READ** each time. Each addition should reflect approximately 100% recovery.
- h. After completing the sequence, the display will show the extrapolated concentration value and the "best-fit" line through the standard additions data points, accounting for matrix interferences.
- i. See Section 1.4.1 *Standard Additions* for more information.

### Method Performance

#### Precision

Standard: 1.000 mg/L  $\text{PO}_4^{3-}$

Program	95% Confidence Limits
3025	0.979–1.021 mg/L $\text{PO}_4^{3-}$
3030	0.985–1.014 mg/L $\text{PO}_4^{3-}$

For more information on determining precision data and method detection limits, refer to Section 1.5.

#### Estimated Detection Limit

Program	EDL
3025	0.045 mg/L $\text{PO}_4^{3-}$
3030	0.031 mg/L $\text{PO}_4^{3-}$

For more information on derivation and use of Hach's estimated detection limit, see Section 1.5.2. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section 1.5.1.

#### Sensitivity

Program Number: 3025

Portion of Curve	$\Delta\text{Abs}$	$\Delta\text{Concentration}$
0.010 Abs	0.010	0.0168 mg/L
1.25 mg/L	0.010	0.0177 mg/L
2.25 mg/L	0.010	0.0185 mg/L

Program Number: 3030

Portion of Curve:	$\Delta\text{Abs}$	$\Delta\text{Concentration}$
0.010 Abs	0.010	0.0160 mg/L
1.1 mg/L	0.010	0.0193 mg/L
1.98 mg/L	0.010	0.0184 mg/L

See Section 1.5.3 *Sensitivity Explained* for more information.

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## **PHOSPHORUS, Reactive (Orthophosphate), continued**

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### **Calibration Standard Preparation**

To perform a phosphate calibration using the ascorbic acid method, use a 10-mg/L Phosphate Standard Solution (Cat. No. 14204-16).

Prepare calibration standards containing 0.300, 1.500, and 2.400 mg/L Phosphate as follows:

- a. Into three different 100-mL Class A volumetric flasks, pipet 3, 15, and 24 mL of the 10-mg/L Phosphate Standard Solution using Class A glassware.
- b. Dilute to the mark with deionized water. Mix thoroughly.
- c. Using the ascorbic acid method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

### **Summary of Method**

Orthophosphate reacts with molybdate in an acid medium to produce a Phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

### **Safety**

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to *Section 1*.

### **Pollution Prevention and Waste Management**

Please see *Section 1* for more information on proper disposal of these materials.

### **5.5 ENTEROLERT<sup>®</sup> PROCEDURES**

#### Introduction:

*Enterolert*<sup>®</sup> is used for analyzing marine water samples starting in the 2006 field season. *Enterolert*<sup>®</sup> detects enterococci such as *E. faecium* and *E. faecalis* at 1 cfu/100 ml. Same methods as *Colilert*<sup>®</sup>, except saltwater is diluted 1:10 and samples are incubated at 41 °C for 24 hours. Results from MPN table are multiplied by the dilution factor.

#### Equipment:

Barnstead Incubator, 35 °C ± 0.5 °C  
*IDEXX* Quanti-tray Sealer  
Rubber Inserts, Quanti-Tray and Quanti-Tray/2000  
365 nm Ultra Violet Lamp

#### Methodology *Enterolert*<sup>®</sup>:

<b>Appearance</b>	<b>Result</b>
Lack of fluorescence	Negative for enterococci
Blue fluorescence	Positive for enterococci

#### Proper Disposal:

All trays testing positive are placed in an autoclave for 30 minute sterilization and then properly disposed.



## 5.6 TRAINING DOCUMENTATION

### MERI Training Documentation Blue Hill Bay Coastal Monitoring Program

Training to be provided by MERI Coastal Monitoring Coordinator to all new staff and interns involved with the monitoring program. New staff members must satisfactorily complete all aspects of this training schedule and then be supervised by a experienced coworker for a period of four weeks before they will be authorized to independently perform field monitoring, sample collection or laboratory analysis.

Employee Name: \_\_\_\_\_ Title: \_\_\_\_\_

Training	Objective	Evaluation
General Laboratory Safety	Identify location and understand operation of fire extinguishers, eye wash stations, fume hoods, protective gear, and chemical storage cabinets	N/A
MSDS	Understand the MSDS system and know where all data sheets are kept in the lab	N/A
Proper Waste Disposal	Be familiar with the procedure for hazardous waste storage and disposal	N/A
EPA Sample Collection Technique	Understand the methods and purpose of the EPA standard operating procedure for field sample collection	Successfully collect field samples following the EPA method
<i>YSI DataSonde</i>	Become comfortable with all aspects of <i>YSI DataSonde</i> operation including data collection/transfer and instrument calibration	Calibrate all probes, create a surveyor data file, perform in-situ measurements, successfully download data
<i>TidbiT</i> ® Loggers	Understand methods for programming logger and data transfer	Launch logger and transfer data via optic shuttle
Nutrient Analysis	Understand the procedures for nitrate and phosphate analysis including spectrophotometer operation	Successfully perform nitrate and phosphate analysis achieving < 10% error on matrix standards
<i>Enterolert</i> ®	Completely understand the <i>Enterolert</i> ® method for bacterial analysis, including biohazard disposal	Perform <i>Enterolert</i> ® procedure and achieve < 10% difference on replicate samples
Record Keeping	Be familiar with field/lab data sheets	N/A
Data Management/ Data Entry	Become comfortable with Excel, google docs and Access database programs	Be able to successfully enter data and navigate programs
QAPP	Thoroughly understand all aspects of the Quality Assurance Project Plan	Agree to adhere to all goals set forth in the QAPP

Employee Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Coastal Monitoring Coordinator: \_\_\_\_\_ Date: \_\_\_\_\_

## 5.7 FIELD DATA SHEET

Blue Hill Bay Coastal Monitoring Study  
Marine Environmental Research Institute (MERI), Blue Hill, ME, 04814 Contact Personnel: Meggan Dwyer Email: mdwyer@meriresearch.org

Field Data - Water Quality- Salt Water Date: \_\_\_\_\_ Name: \_\_\_\_\_ High Tide: \_\_\_\_\_

Site Name	Time Monitored	Temp(°C)	Cond (mS/cm)	Salinity (ppt)	pH	Turbidity (NTU)	Chl $\alpha$ ( $\mu$ g/L)	DO % mg/L	Nutrient samples Collected? (check if yes)
Country Club									
Golf Course									
Country Club Beach*									
Salt Pond									
South Blue Hill									
ABC #									
Bachelders Brook*									
Naskeag									
Great Marsh									
Inner Salt Pond *									
Peter Cove *									
KYC Dock* #									
McHeards Cove									
Curtis Cove *									
Carter Preserve *									
Carrying Place *									
Surry Wharf									
Blue Hill Park *									

\* Collect Bacteria samples weekly # Collect Phytoplankton samples weekly  
Collect Nutrient samples monthly at all locations

## 5.7 SAMPLE COLLECTION METHOD

Adapted from U.S. EPA, Volunteer Stream Monitoring, A Methods Manual  
EPA 841-B-97-003. November, 1997

Reused sample containers and glassware must be cleaned and rinsed before the first sampling run and after each run by following either Method A or Method B described below. The most suitable method depends on the parameter being measured.

### Acid Wash Procedure for Preparing Sampling Containers

This method should be used when preparing all sample containers and glassware for monitoring nitrates and phosphorus. Wear latex gloves!

1. Wash each sample bottle or piece of glassware with a brush and phosphate-free detergent.
2. Rinse three times with cold tap water.
3. Rinse with 10 percent hydrochloric acid.

4. Rinse three times with deionized water.

### **Sample Collection Technique**

In general, sample away from the stream bank in the main current. Never sample stagnant water. The outside curve of the stream is often a good place to sample, since the main current tends to hug this bank. In shallow stretches, carefully wade into the center current to collect the sample.

A boat will be required for deep sites. Try to maneuver the boat into the center of the main current to collect the water sample. When collecting a water sample for analysis in the field or at the lab, follow the steps below.

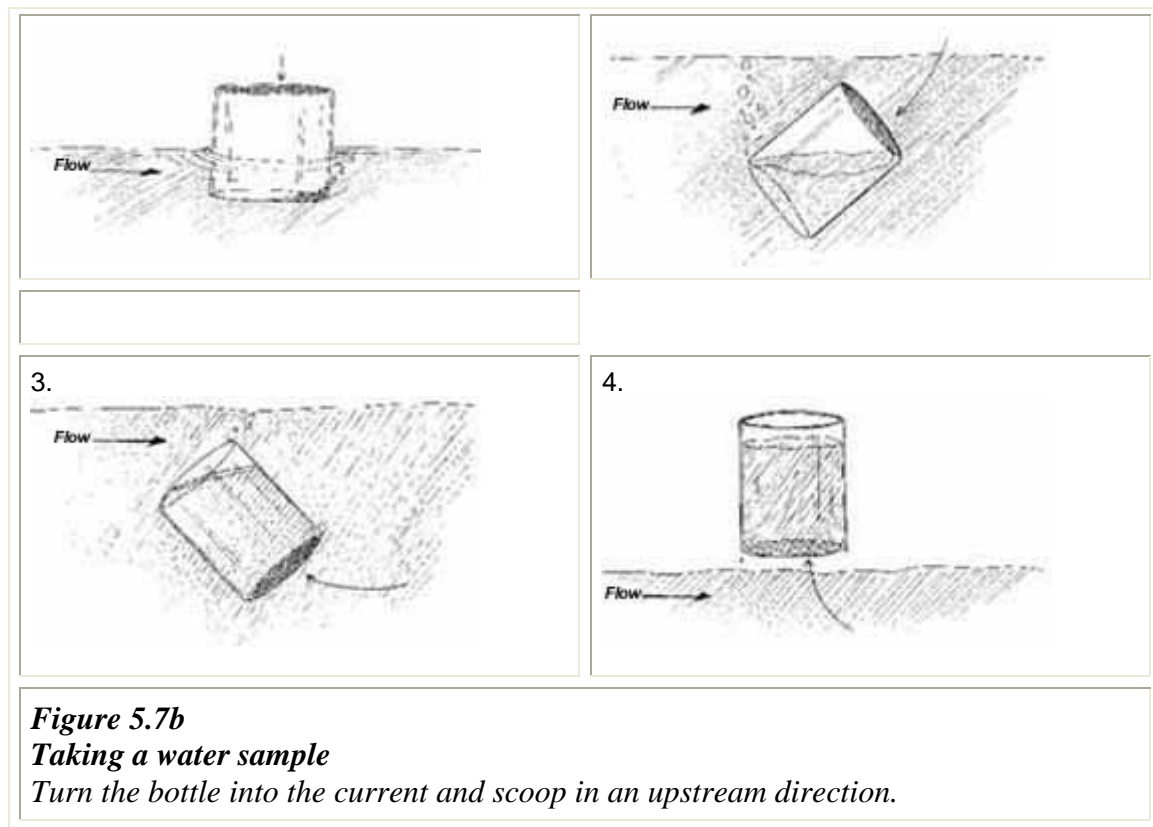
To collect water samples using screw-cap sample bottles, use the following procedures (Fig. 5.7a and 5.7b):



**Figure 5.7a**  
***Getting into position to take a water sample***  
*Sample in the main current, facing upstream.*

1.

2.



1. Label the bottle with the site name and date.
2. Remove the cap from the bottle just before sampling. Avoid touching the inside of the bottle or the cap. If you accidentally touch the inside of the bottle, use another one.
3. *Wading.* Try to disturb as little bottom sediment as possible. In any case, be careful not to collect water that has sediment from bottom disturbance. Stand facing upstream. Collect the water sample on your upstream side, in front of you. You may also tape your bottle to an extension pole to sample from deeper water. *Boat.* Carefully reach over the side and collect the water sample on the windward side of the boat.
4. Hold the bottle near its base and plunge it (opening downward) below the water surface. If you are using an extension pole, remove the cap, turn the bottle upside down, and plunge it into the water, facing upstream. Collect a water sample 8 to 12 inches beneath the surface or mid-way between the surface and the bottom if the stream reach is shallow.
5. Turn the bottle underwater into the current and away from you. In slow-moving stream reaches, push the bottle underneath the surface and away from you in an upstream direction.

6. Leave a 1-inch air space. Do not fill the bottle completely (so that the sample can be shaken just before analysis). Recap the bottle carefully, remembering not to touch the inside.
7. If the samples are to be analyzed in the lab, place them in the cooler with 2 ice packs for transport to the lab.