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# Great Bay Estuary Tidal Tributary Monitoring Program (GBETTMP) 2013-2017 Quality Assurance Project Plan

New Hampshire Department of Environmental Services

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*New Hampshire Department of Environmental Services*

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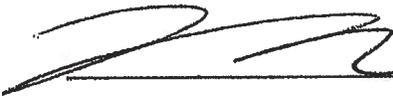
**Great Bay Estuary Tidal Tributary Monitoring Program  
(GBETTMP) 2013 - 2017**

**Quality Assurance Project Plan**

**July 22, 2013**

*Prepared by*  
**Matthew A. Wood, Project QA Officer**  
**NH Department of Environmental Services**  
**Watershed Management Bureau**

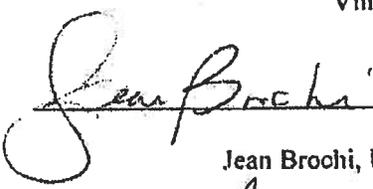
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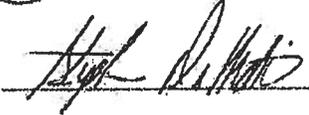
Project Manager:  8/9/13  
Signature / Date  
Philip Trowbridge, PREP/DES

Project QA Officer:  8/9/13  
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Matthew A. Wood, DES

Laboratory Manager:  8/9/13  
Signature / Date  
Jody Potter, UNH-WQAI.

DES QA Manager:  8/9/13  
Signature / Date  
Vincent Perelli, DES

USEPA Project Manager:  8/2/13  
Signature / Date  
Jean Brochi, US EPA Region I

USEPA QA Manager:  07/04/13  
Signature / Date  
Stephen DiMattei, US EPA Region I

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### A3 – Distribution List

Table 1 presents a list of people who will receive the approved QAPP, any QAPP revisions, and any amendments.

**Table 1: QAPP Distribution List**

QAPP Recipient Name	Project Role	Organization	Telephone Number and E-mail Address
Phil Trowbridge	Project Manager	PREP/DES	603-271-8872 <a href="mailto:Philip.Trowbridge@des.nh.gov">Philip.Trowbridge@des.nh.gov</a>
Matthew A. Wood	Project QA Officer	DES	603-271-8868 <a href="mailto:Matthew.Wood@des.nh.gov">Matthew.Wood@des.nh.gov</a>
Bill McDowell	Laboratory Program Manager	UNH	603-862-2249 <a href="mailto:Bill.McDowell@unh.edu">Bill.McDowell@unh.edu</a>
Jody Potter	Laboratory Manager	UNH-WQAL	603-862-2341 <a href="mailto:Jody.Potter@unh.edu">Jody.Potter@unh.edu</a>
Michelle Daley	Field Operations Manager	UNH	603-862-2341 <a href="mailto:Michelle.Daley@unh.edu">Michelle.Daley@unh.edu</a>
Jean Brochi	EPA Project Manager	USEPA New England	617-918-1536 <a href="mailto:Brochi.Jean@epa.gov">Brochi.Jean@epa.gov</a>
Stephen DiMattei	EPA Quality Assurance Officer	USEPA New England	617-918-8369 <a href="mailto:dimattei.steve@epa.gov">dimattei.steve@epa.gov</a>
Vince Perelli	DES QA Manager	DES	603-271-8989 <a href="mailto:Vincent.Perelli@des.nh.gov">Vincent.Perelli@des.nh.gov</a>

### A4 – Project/Task Organization

The Piscataqua Region Estuaries Partnership (PREP) is part of the U.S. Environmental Protection Agency’s National Estuary Program, which is a joint local/state/federal program established under the Clean Water Act with the goal of protecting and enhancing nationally significant estuarine resources. The PREP receives its funding from the EPA and is administered by the University of New Hampshire.

The project will be conducted and managed by PREP. The Project Manager (Phil Trowbridge) will be responsible for coordinating all program activities.

The Field Operations Manager (Michelle Daley) will manage all field staff, be responsible for “stop/go” decisions for daily sampling runs during extreme events, and will notify the Laboratory Manager when samples will be delivered. The Field Operations Manager will be responsible for resolving any logistical problems and communicating the results to the field staff.

Samples will be analyzed by the Water Quality Analysis Laboratory (WQAL) at the University of New Hampshire (UNH). Laboratory operations will be managed by the Laboratory Manager (Jody Potter) and overseen by the Laboratory Program Manager (Bill McDowell). The Laboratory Manager will be responsible for conducting analyses according to the procedures in this QA Project Plan, identifying any non-conformities or analytical problems, and reporting any problems to the Laboratory

Program Manager, Project QA Officer, and the Project Manager. The Laboratory Program Manager will be responsible for resolving any problems and communicating the results to the laboratory staff.

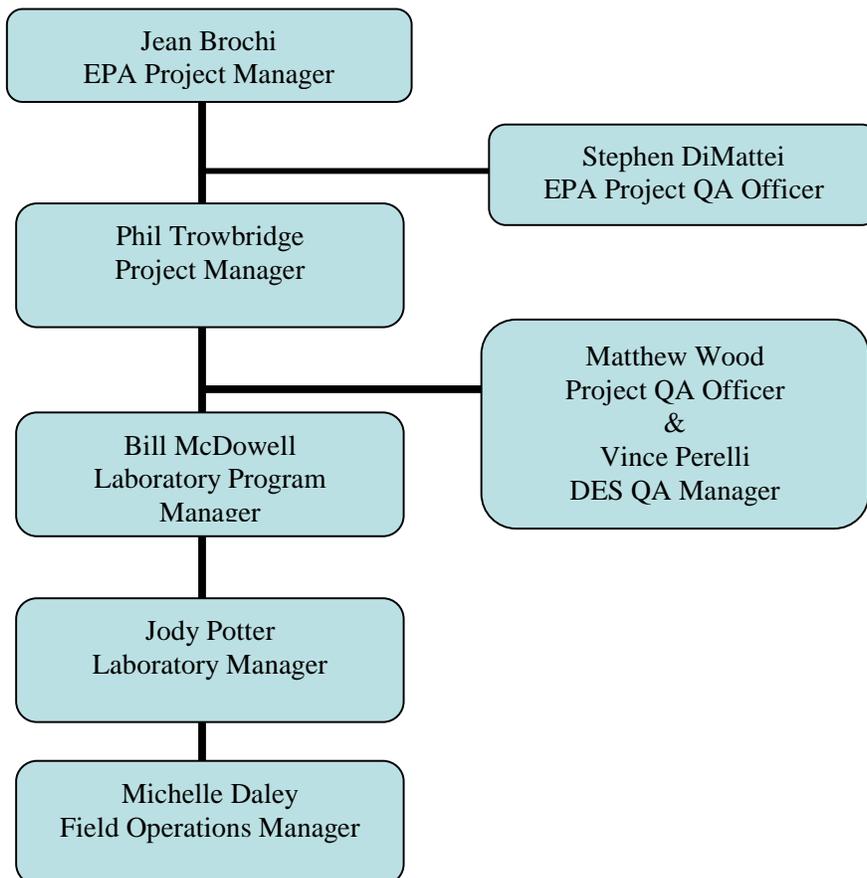
At the end of the project, the Project QA Officer (Matthew A. Wood) will review the results of QA/QC checks and verify that the procedures of this QA Project Plan were completed. The Project QA Officer will be responsible for a memorandum to PREP summarizing any deviations from the procedures in the QA Project Plan, the results of the QA/QC tests, and whether the reported data meets the data quality objectives of the project.

Funding for PREP is provided by the U.S. Environmental Protection Agency. Therefore, the Project Manager will be accountable to the EPA Project Manager (Jean Brochi) and the EPA Project QA Officer (Stephen DiMattei). The EPA Project Manager and EPA Project QA Officer will be responsible for approving the Quality Assurance Project Plan. The DES QA Manager (Vince Perelli) is responsible for reviewing and approval of the QA Project Plan before submittal to EPA.

The principal user of the data from this project will be PREP for State of Our Estuaries Reports. The Project Manager will prepare a report for PREP at the end of the project with all the data and the QA Officer's summary report.

Figure 1 shows an organizational chart for this project.

**Figure 1: Project Organization**



## A5 – Problem Definition/Background

Nitrogen enrichment is a growing concern for the Great Bay Estuary. In the 2013 State of Our Estuaries report (PREP, 2013), PREP calculated the nitrogen load from tributaries to the Great Bay Estuary using data collected by UNH for the Great Bay Estuary Tidal Tributary Monitoring Program. PREP needs to update this indicator for future State of Our Estuaries reports. Therefore, the purpose of this study is to continue to collect representative data on the concentrations of total nitrogen and other parameters in ambient water in tributaries to the Great Bay Estuary in 2013 through 2017. Nitrate+nitrite (NO<sub>2</sub>/NO<sub>3</sub>), ammonia (NH<sub>4</sub>), total dissolved nitrogen (TDN), particulate nitrogen (PN), total nitrogen (TN), total phosphorus (TP) and total suspended solids (TSS) will be measured in the water samples.

The study design will follow the tributary sampling design which was implemented by the New Hampshire Department of Environmental Services (DES) between 2001 and 2007, and continued by PREP between 2008 and 2012. The Sampling design is described in Section B of this QAPP (DES, 2008). Grab samples will be collected from eight tributaries monthly from March to December of each year. One sample from each month will be replicated for QA purposes (>10% of samples). The samples will be analyzed by the Water Quality Analysis Laboratory at the University of New Hampshire. PREP decided to change the laboratory for this program for 2008 to 2012 from DES to the University of New Hampshire in order to save money and reduce staff time needed to transport samples from the seacoast to Concord, NH. The analytical methods used at the UNH lab are not the same as those used by DES. However, a laboratory comparability project conducted in 2008 demonstrated that the different methods produce fully comparable results.

The TN concentrations in each river will be matched with the daily average streamflow for that river. Stream flow data will be obtained from permanent USGS stream gages. The drainage area ratio method will be used to estimate stream flows for sampling locations that are not coincident with USGS stream gages. The USGS LOADEST statistical program will be used to estimate annual average TN loads from each tributary.

This sampling program will continue for at least five years, starting in 2013 and ending in 2017.

## A6 – Project/Task Description

The tasks and schedule for the project in 2013 are summarized in Table 2. The sample collection, analysis, and reporting tasks will follow a similar schedule in 2014 through 2017.

**Table 2: Project Schedule Timeline**

Activity	Dates		Product	Due Date
	Anticipated Date(s) of Initiation	Anticipated Date(s) of Completion		
QAPP Preparation	04/22/13	06/01/13	QAPP Document	06/01/13
Training	03/11/13	03/15/13	Field crews trained on SOPs	03/28/13
Sample collection	03/28/13	12/18/13	Nutrient samples collected, delivered to laboratory, and stored	12/18/13
Sample analysis	03/28/13	12/18/13	Laboratory analyses for nutrient samples completed	02/28/14

Activity	Dates		Product	Due Date
	Anticipated Date(s) of Initiation	Anticipated Date(s) of Completion		
Laboratory Report	01/01/14	01/31/14	Report from the Laboratory Manager with the final, quality-assured results for tributary samples and QC samples	02/28/14
Data Quality Audit	03/01/14	03/15/14	Memo from QA Project Officer summarizing results of QC samples and QAPP nonconformances	03/15/14
Annual Report	02/16/14	03/31/14	Final project report	03/31/14

### A7 – Quality Objectives and Criteria

Table 3 summarizes the performance criteria for the NO<sub>2</sub>/NO<sub>3</sub>, NH<sub>4</sub>, TDN, PON, TN, TP, and TSS samples that will be collected for this project. More details on each data quality objective are provided in the paragraphs below the table.

**Table 3: Measurement Performance Criteria for Laboratory Samples**

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance
Precision-Overall	RPD < 30%	Field Duplicates
Precision-Lab	RPD < 15%	Lab Duplicates
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples
Comparability	Measurements should follow standard methods that are repeatable	NA
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA
Data Completeness	Valid data for 90% of planned samples (9 samples at each tributary)	Data Completeness Check

**Precision:** Relative percent difference (RPD) of duplicate samples is used as one index of precision for nutrient analyses. This is defined as the absolute difference between the duplicates divided by the average of the duplicates. For laboratory duplicates, a difference greater than 10% requires further investigation of the sample run. A difference greater than 15% is failure (unless the average of the two samples is less than 10X the MDL), and results in reanalysis of the entire sample queue, unless there is a reasonable and supported explanation for the inconsistency. For field duplicates, a difference greater

than 30% will be flagged as a potential error. Duplicate precision will be analyzed by calculating the RPD using the equation:

$$RPD = \frac{|x_1 - x_2|}{\left(\frac{x_1 + x_2}{2}\right)} \times 100\%$$

where  $x_1$  is the original sample concentration  
 $x_2$  is the duplicate sample concentration

Accuracy/Bias. For nutrient analyses, certified reference materials are analyzed periodically (approximately every 20 samples) in each sample queue to assure accuracy. Generally, a RPD from the certified concentration of more than 10% requires further investigation of that run. A difference greater than 15% is failure (unless the average of the two samples is less than 10X the MDL), and results in reanalysis of the entire sample queue, unless there is a reasonable and supported explanation for the inconsistency. RPDs for certified reference materials will be calculated using the following equation:

$$RPD = \frac{|x_1 - x_2|}{(x_2)} \times 100\%$$

where  $x_1$  is the measured concentration  
 $x_2$  is the known concentration for the certified reference material

Laboratory Fortified Matrix samples are also used to assess accuracy of nutrient analyses. The difference of the spiked sample concentration (SA) minus the unspiked sample concentration (SU) divided by the known concentration added (A) (expressed as percent) gives percent recovery (R):

$$R = \frac{(SA - SU)}{A} \times 100\%$$

Generally, a recovery <90% or >110% requires further investigation of the sample run. A recovery greater than or less than <85% or >115% is failure (unless the sample is less than 10X the MDL), and results in reanalysis of the entire sample queue, unless there is a reasonable and supported explanation for the inconsistency

Representativeness: The samples will be taken at the same locations and using the same methods as used for the GBETTMP sampling in 2008-2012 if possible. Any necessary changes to sampling locations will be made with the Field Operations Manager's approval, with the goal of reproducing the original location as effectively as possible. Any such changes will be fully documented in project reports

Comparability: Standardized field and analytical methods will be used. These methods will follow the current industry standard for the types of measurements being taken. Written SOPs will be followed for field and analytical measurements. Standardized field data sheets will be used. PREP has completed lab comparability tests to verify that the laboratory methods proposed for this study will produce comparable data as the DES laboratory. The DES laboratory performed the laboratory analyses for this program from 2001 through 2007.

**Sensitivity:** The laboratory methods used should be capable of detecting NO<sub>2</sub>/NO<sub>3</sub>, NH<sub>4</sub>, TDN, PON, TN, TP, and TSS concentrations in ambient river water. In October, November, and December 2007, 30 samples were collected from the tributary stations to test the laboratory methods. The ranges of results for TDN, TP, and TSS were 0.21-2.03, 0.007-0.204, and 1.05-5.41 mg/L, respectively. These results are all greater than or equal to the method detection levels listed in Table 9.

**Completeness:** This study will be deemed successful if data meeting the data quality objectives is obtained for 90% of planned samples (not including field/laboratory duplicates). Therefore, at least nine valid results for each parameter should be obtained from each tributary.

### A8 – Special Training/Certification

The Field Operations Manager will organize and implement a training session for field staff. The training session will cover SOPs for field instruments and field data sheets. The training will be based on the QAPP document. Field staff will sign an attendance sheet for the training, which will be retained by the Field Operations Manager. The training will be completed before sampling begins.

**Table 4: Special Personnel Training Requirements**

Project Function	Description of Training	Training Provided by	Training Provided to	Location of Training Records
Water quality sampling and field measurements	Sampling methods in Section B2 and field data sheets. This training will be conducted once at the beginning of the field season.	Field Operations Manager	All field team staff	With Field Operations Manager

### A9 – Documents and Records

**QA Project Plan**

The Project Manager will be responsible for maintaining the approved QA Project Plan and for distributing the latest version to all parties on the distribution list in section A3. A copy of the approved plan will be posted to the PREP website ([www.prep.unh.edu](http://www.prep.unh.edu)).

**Field Data Sheets**

The field data sheets for this project are attached as Appendix B. Field crews fill in these forms during the day and return them to the Field Operations Manager upon completion. The original forms, or scanned copies of the original forms will be retained on file by the Field Operations Manager.

**Laboratory Data Sheets**

Data packages from the Laboratory Manager to the Project Manager will be electronic laboratory data sheets containing the results of analyses plus the results of QC tests performed. See Appendix A Section VI for details of laboratory electronic and paper records maintained by the laboratory.

**Reports to Management**

The Project QA Officer will produce an annual report for PREP. The final work product will be an Excel spreadsheet containing quality assured results of the laboratory analyses for each station on

each date and an annual report describing any deviations from the protocols established in the QA Project Plan. The annual report will be posted to the PREP website ([www.prep.unh.edu](http://www.prep.unh.edu)).

**Archiving**

The QA Project Plan and final report will be kept on file at PREP and DES for a minimum of 10 years after the publication date of the final report. The original field data sheets, or scanned copies of the original field data sheets will be retained by the Field Operations Manager and laboratory data sheets will be retained by the Laboratory Manager for a minimum of 5 years.

**B1 – Sampling Process Design**

Eight tributaries to the Great Bay Estuary watershed will be sampled ten times for nitrate+nitrite (NO<sub>2</sub>/NO<sub>3</sub>), ammonia (NH<sub>4</sub>), total dissolved nitrogen (TDN), particulate nitrogen (PN), total phosphorus (TP) and total suspended solids (TSS). One water sample will be collected as a grab from the head-of-tide station for each of the tributaries on each day of sampling. A total of ten field duplicate samples will be collected during the year for each parameter (one station per sampling date). Table 5 shows the number of samples that will be collected for each parameter. The critical parameters for this study are NO<sub>2</sub>/NO<sub>3</sub>, NH<sub>4</sub>, TDN, PN, TN, TP, and TSS. Water temperature, dissolved oxygen, pH and specific conductance will be measured for information only.

Ten of the field duplicate samples collected as part of the sampling design will be analyzed for total nitrogen (TN) using USGS Method I-4650-03. The results of the TN analysis will be compared to calculated TN values (TN-calculated) derived by summation of TDN and PN. This paired analysis will be used to verify the new USGS nationally recommended methods (Office of Water Quality Technical Memorandum 2013.01) and confirm that the previous data remain valid.

The stations that will be sampled as part of this study are provided in Table 6. A map of the stations is provided in Figure 2.

The sampling dates for 2013 and station for the field duplicate sample are shown in Table 7. The dates for sampling in 2014 through 2017 will be determined by field crews in February of each subsequent year.

**Table 5: Sample Summary**

Parameter	No. of Stations	Samples per Event per Site	Number of Sampling Events	Field Duplicate Samples	Total Number to Lab
NO <sub>2</sub> /NO <sub>3</sub>	8	1	10	10	90
NH <sub>4</sub>	8	1	10	10	90
TDN	8	1	10	10	90
PN	8	1	10	10	90
TN	0	0	0	10 (field dupes of samples also analyzed for TDN and PN)	10
TP	8	1	10	10	90

Parameter	No. of Stations	Samples per Event per Site	Number of Sampling Events	Field Duplicate Samples	Total Number to Lab
TSS	8	1	10	10	90
Water Temperature	8	1	10	10	0 (field measurement)
Dissolved Oxygen Concentration	8	1	10	10	0 (field measurement)
Dissolved Oxygen Saturation	8	1	10	10	0 (field measurement)
pH	8	1	10	10	0 (field measurement)
Specific Conductance	8	1	10	10	0 (field measurement)

**Table 6: Tributary Sample Locations**

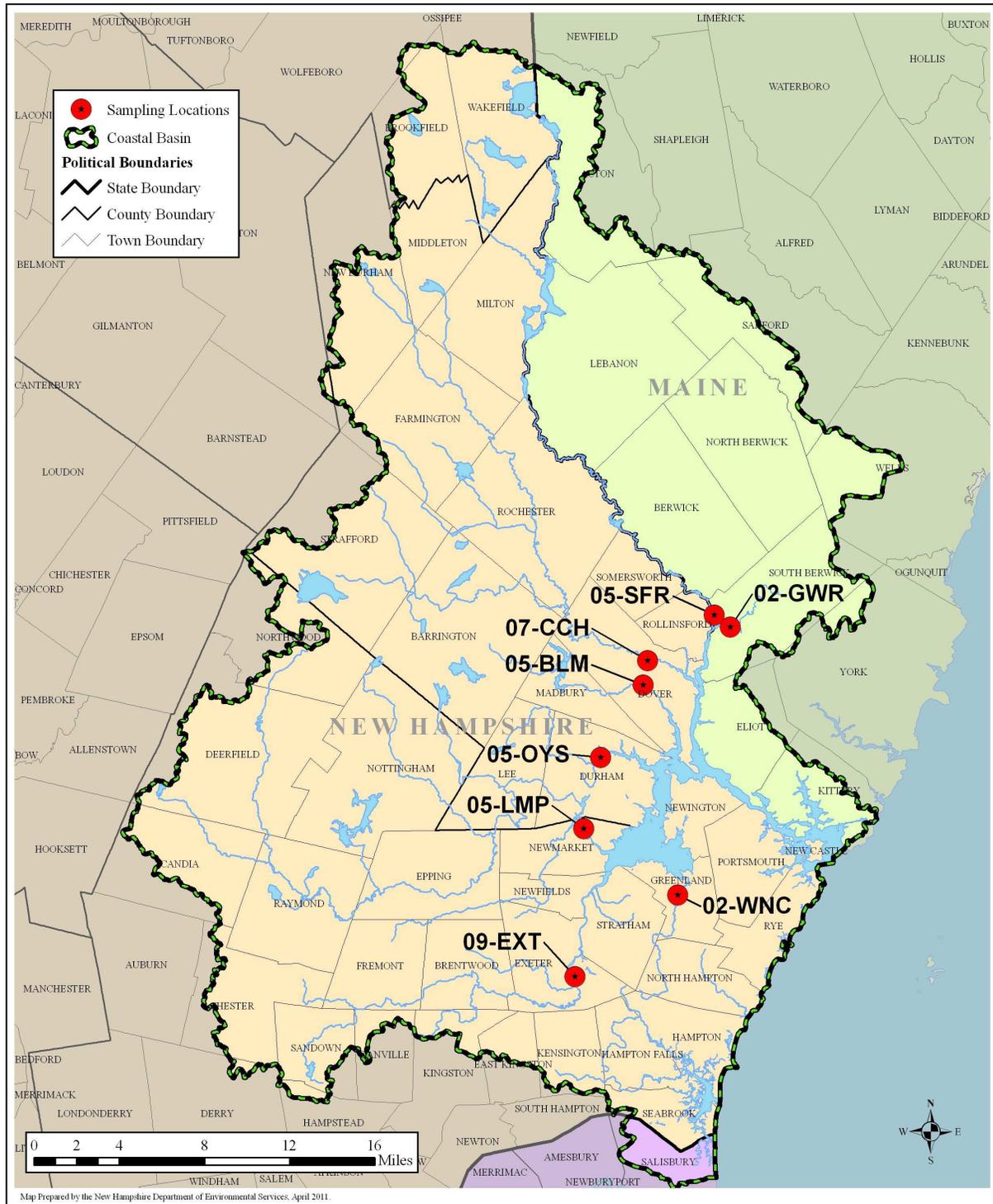
Station ID / Tributary	Town, State	Latitude	Longitude	Sample Location
02-GWR Great Works	South Berwick, ME	43.2189	-70.7967	Route 236 in south Berwick ME, turn right onto Brattle Street, sample on downstream side of Brattle street bridge.
05-SFR Salmon Falls	Rollinsford, NH	43.2272	-70.8115	Rte 4 bridge in Rollinsford NH, sample on upstream side of bridge
07-CCH Cocheco	Dover, NH	43.1965	-70.8741	Rte 9 bridge in Dover. Central Ave between Washington St and Portland Ave. sample on upstream side, midway on bridge.
05-OYS Oyster	Durham, NH	43.1309	-70.9186	Rte 108 bridge in Durham NH. Sample from top of fish ladder on river left side, upstream of dam.
05-LMP Lamprey	Newmarket, NH	43.0821	-70.9350	Rte 108 bridge in Newmarket NH. Sample on upstream side at midpoint of the bridge.
09-EXT Exeter	Exeter, NH	42.9820	-70.9455	High Street bridge in Exeter NH. Sample on downstream side at midpoint of bridge.
05-BLM Bellamy	Dover, NH	43.1799	-70.8782	Rte 108 bridge in Dover. Sample on downstream side at midpoint of bridge.
02-WNC Winnicut	Greenland, NH	43.0361	-70.8480	Route 33 bridge in Greenland NH. Sample on downstream side at midpoint of bridge.

**Table 7: Sampling Schedule for 2013**

Month	Day of Week	Date	Station for Duplicate Sample
March	4 <sup>th</sup> Thursday	3/28/13*	02-GWR
April	4 <sup>th</sup> Wednesday	4/24/13*	02-WNC
May	4 <sup>th</sup> Wednesday	5/22/13*	09-EXT
June	3 <sup>rd</sup> Wednesday	6/19/13*	05-LMP
July	3 <sup>rd</sup> Wednesday	7/17/13*	05-OYS
August	3 <sup>rd</sup> Wednesday	8/21/13	07-CCH
September	3 <sup>rd</sup> Wednesday	9/18/13	05-BLM
October	3 <sup>rd</sup> Wednesday	10/16/13	05-SFR
November	4 <sup>th</sup> Wednesday	11/27/13	05-LMP
December	3 <sup>rd</sup> Wednesday	12/18/13	05-OYS

\*Protocols from the 2008-2012 QAPP (DES, 2008) will be followed until approval of the 2013-2017 QAPP

Figure 2: Sampling locations in the Great Bay Estuary Watershed, Coastal Basin



## B2 – Sampling Methods

### Sample Bottle Preparation

Two-liter Nalgene bottles are prepared before sampling by soaking bottles and caps in a 10% HCl solution for 10 minutes. Bottles and caps are subsequently rinsed with deionized water six times and air dried before being stored. During higher spring/fall flow, one bottle is prepared for each site. During low summer flow, two bottles are prepared for each site. Before field sampling day, bottles are labeled with StationID, date, and program (“GBETTMP”) and placed in a cooler for transfer and storage.

### Water Sampling Field Procedures

All field measurements and samples collected for laboratory analyses are collected using a two-gallon bucket on a rope using the following procedure:

1. The bucket will be lowered from the middle of the bridge at the station down to the river. The bucket will be immersed three times in the river before it is filled and hauled up. The bucket will be filled to at least one-half of its capacity, which ensures sufficient volume for all field measurements and sample storage containers. This is considered a surface grab sample since the bucket sampling technique collects water from the top 1 foot of the water column.
2. The sample for laboratory analysis will be immediately filled by pouring water from the bucket into the individual sample storage container(s) (i.e., polyethylene bottles, pre-labeled with the stationID, date, time, and program). The bucket should be shaken to fully mix the water before the water is poured off into the sample bottle.
3. If a field duplicate sample is needed at the station, the bucket will be emptied and then refilled from the river following Step 1. The field duplicate sample will be filled following Step 2. Duplicate field parameters will be measured following steps 4 and 5.
4. The sample bottle(s) will be placed in a cooler with ice for transport to the laboratory.
5. The bucket will be emptied and then refilled from the river following Step 1 for field parameter measurements.
6. Field parameters will be measured in a new bucket of water using a YSI multiparameter meter by inserting the temperature/specific conductance probe in the bucket and moving the probe slowly for 15-30 seconds until the temperature and specific conductance values stabilize. Field parameters may also be measured directly from the river if accessible.
7. The results of the field parameters and any comments relevant to the sampling event (e.g., sampling and/or instrumentation problems) will be documented on field data sheets (Appendix B) prior to traveling to the next sampling location.

This procedure is repeated at all scheduled sampling locations for a particular day. Field teams are responsible for reporting sampling method problems to the Field Operations Manager who is responsible for taking corrective action.

Documentation of field methods used between March 28 and July 17, 2013 are described in Appendix F.

**Table 8: Sample Requirements**

Analytical Parameter	Collection Method	Sampling SOP	Sample Volume	Container Size and Type	Preservation Requirements	Max. Holding Time (Preparation and Analysis)
NO <sub>2</sub> /NO <sub>3</sub>	Grab	Section B2	60 mL	2000 ml HDPE	Subsample 60 mL of	Indefinite once

Analytical Parameter	Collection Method	Sampling SOP	Sample Volume	Container Size and Type	Preservation Requirements	Max. Holding Time (Preparation and Analysis)
				bottle (same bottle for all analyses)	unfiltered water and freeze within 8 hours of sample collection	frozen
NH <sub>4</sub>	Grab	Section B2	60 mL	2000 ml HDPE bottle (same bottle for all analyses)	Subsample 60 mL of unfiltered water and freeze within 8 hours of sample collection	Indefinite once frozen
TDN	Grab	Section B2	60 mL	2000 ml HDPE bottle (same bottle for all analyses)	Filter a 60 mL subsample into a HDPE bottle and freeze within 8 hours of sample collection	Indefinite once frozen
PN	Grab	Section B2	~1,600 mL	2000 ml HDPE bottle (same bottle for all analyses)	Dry filter (See Appendix D)	Indefinite once dried
TN	Grab	Section B2	60 mL	2000 ml HDPE bottle (same bottle for all analyses)	Subsample 60 mL of unfiltered water and freeze within 8 hours of sample collection	Indefinite once frozen
TP	Grab	Section B2	60 mL	2000 ml HDPE bottle (same bottle for all analyses)	Subsample 60 mL of unfiltered water and freeze within 8 hours of sample collection	Indefinite once frozen
TSS	Grab	Section B2	~1,600 mL	2000 ml HDPE bottle (same bottle for all analyses)	Dry filter (See Appendix D)	7 days
Field Parameters (measurements made in the field)						
Temperature	Surface Grab	YSI multiparameter meter manual	NA	NA	NA	NA
Specific Conductance	Surface Grab	YSI multiparameter meter manual	NA	NA	NA	NA
pH	Surface Grab	YSI multiparameter meter manual	NA	NA	NA	NA
Dissolved Oxygen	Surface Grab	YSI multiparameter meter manual	NA	NA	NA	NA

### B3 – Sample Handling and Custody

Upon collection, nutrient samples will be transported on ice in a cooler until they arrive at WQAL. Samples will be delivered to WQAL by 15:00 on the sampling date. Sample login and handling procedures at WQAL are described in Section IV of Appendix A. Immediately after login, a portion of the sample will be filtered following the procedure below.

**Filtration:** Particulate material is separated from dissolved constituents via filtration in the laboratory immediately upon delivery to the laboratory (normally within 5 hours of collection). For total dissolved nitrogen, a portion of the original sample (approx. 60 mL) is filtered through 47mm Whatman GF/F glass fiber filters (nominal pore size of 0.70µm) in the field, collected in a pre-washed HDPE bottle, and then immediately frozen. For total suspended sediments and particulate nitrogen, a portion of the original sample (generally 500-1900 mL) is processed using the filtration procedures in Appendix D with two pre-weighed glass fiber filters (25 mm Whatman GF/F). One of these filters is analyzed for both TSS and PN. The other filter is stored as backup for the PN analysis.

GF/F filters (nominal pore size of 0.70µm) are commonly used in nutrient studies for filtering particulates from water samples, for example, National Coastal Assessment uses 0.7 um filters for dissolved nutrient analysis, as does the Maryland Chesapeake Bay Water Quality Monitoring Program. GF/F filters have been will be used for this study because this type of filter is able to be combusted prior to use to remove traces of C and N to reduce contamination of samples. After filtration, the sample will be frozen at -20°C.

### B4 – Analytical Methods

Appendix A is the QA Plan for the UNH Water Quality Analysis Laboratory. This document describes the general SOPs for the laboratory. This QA plan has been included with other QAPPs that have been approved by EPA Region I.

Laboratory analytical methods for this study are described in detail in Appendices C, D, E, G, H and I. Appendix C contains the SOP for TDN concentrations. Appendix D contains the protocol for filtering samples for total suspended solids. Appendix E contains the protocol for the TN and TP using alkaline persulfate digestion. Appendix G contains the SOP for ammonia concentrations. Appendix H contains the SOP for NO<sub>2</sub>/NO<sub>3</sub> concentrations. Appendix I contains the protocol for PN using the EPA method.

The Laboratory Manager is responsible for corrective actions if any problems with the analytical methods arise. Laboratory data reports are expected annually. All data for the project must be delivered from the laboratory to the Project Manager according to the schedule in Table 2.

**Table 9: Surface Water Target Analytes and Reference Limits**

Analyte	Analytical method (See Appendices for SOP details)	Project Action Level	Analytical/Achievable Method Detection Limit	Project Quantitation Limit
NO <sub>2</sub> /NO <sub>3</sub>	USEPA 353.2 Revision 2.0, August, 1993 (App. H)	NA-data will be used for trend analysis	0.005 mg/L	0.005 mg/L
NH <sub>4</sub>	USEPA method 350.1, 1971, modified March 1983 (App. G)	NA-data will be used for trend analysis	0.005 mg/L	0.005 mg/L
TDN	High temperature catalytic oxidation (App. C)	NA-data will be used for trend analysis	0.1 mg/L	0.1 mg/L

Analyte	Analytical method (See Appendices for SOP details)	Project Action Level	Analytical/Achievable Method Detection Limit	Project Quantitation Limit
PN	USEPA Method 440.0 (App. I)	NA-data will be used for trend analysis	0.01 mg/L	0.01 mg/L
TN	USGS Method I-4650-03 Alkaline persulfate digestion (App. E)	NA-data will be used to verify new methods and document previous data remain valid	0.015 mg/L	0.015 mg/L
TN - calculated	Calculated (TDN + PN)	NA-data will be used for trend analysis	NA	NA
TP	USGS Method I-4650-03 Alkaline persulfate digestion (App. E)	NA-data will be used for trend analysis	0.007 mg/L	0.007 mg/L
TSS	APHA Method 2540-D (App. D)	NA-data will be used for trend analysis	1 mg/L	1 mg/L

### B5 – Quality Control

Section VII of Appendix A describes the quality control measures that will be used for nutrient analyses by the UNH Water Quality Analysis Laboratory. Section A7 describes how the data quality objectives will be evaluated.

The Field Operations Manager will verify that the field crews are following the protocols correctly during the field sampling audit (see Section C1).

Databases of results will be checked for transcription errors and bad data using two methods. First, the entire data set will be printed and checked against the entries in each field or laboratory data sheet by the Laboratory Manager. Second, the Project QA Officer will construct box-plots and other graphical tools (such as scatter and timeseries plots) to determine if there are outliers in the data set. The Project QA Officer will report any outliers to the Project Manager, who will determine whether these data should remain in the dataset.

### B6/B7 – Instrument/Equipment Testing, Inspection, Maintenance, Calibration and Frequency

Equipment inspections and maintenance schedules for the laboratory are described in Section IX of Appendix A. Equipment calibration procedures for the laboratory are listed in Section V of Appendix A. Calibration runs are stored in the laboratory database along with the run sheets for environmental samples. Calibration records will be retained by the Laboratory Manager for a minimum of 10 years. For field measurements of specific conductance, the YSI multiparameter meter is checked in the morning before each sampling date to determine if the calibration is still accurate. The sensor is immersed in a

standard of 500 uS/cm. The meter is considered to be in control if the reading is between 475 and 525 uS/cm. For field measurements of pH, the YSI multiparameter meter is calibrated using three pH buffer solutions (4.0, 7.0, and 10.0). For field measurements of DO, the YSI multiparameter meter is put inside the calibration cup with a small amount of tap water, ensured that the DO probe is not touching water and that the cup air is saturated with water, and calibrated to 100% saturation based on the barometric pressure in the lab. The temperature probe readings will be compared to a NIST calibrated thermometer in tap water as part of the field meter calibration procedure annually.

**B8 – Inspection/Acceptance Requirements for Supplies and Consumables**

Quality control procedures for consumables are listed in Section VII of Appendix A.

**B9 – Non-Direct Measurements**

The project will include use of USGS daily average stream flow measurements from stream gages in the Great Bay Estuary Watershed to help estimate annual loading of nitrogen. The data will be downloaded from the USGS website.

**B10 – Data Management**

Field data will be recorded on standard field data sheets. Laboratory data will be transferred from laboratory data sheets to Excel spreadsheets. All laboratory data will be stored electronically in Excel spreadsheets which will be transferred to the Project Manager as part of the laboratory report. The Project Manager will be responsible for uploading the data to the DES Environmental Monitoring Database (which is compatible with EPA’s Water Quality Exchange). The ProjectID for the data will be “GBETTMP” (Great Bay Estuary Tidal Tributary Monitoring Program). Management of hardcopy data and documents is described in Section A9.

**C1 – Assessments and Response Actions**

In order to confirm that field sampling, field analysis and laboratory activities are occurring as planned, the Project Manager, Field Operations Manager, and Laboratory Manager shall confer, after the first sampling event each year, to discuss the methods being employed and to review the quality assurance samples. At this time all concerns regarding the sampling protocols and analysis techniques shall be addressed and any changes deemed necessary shall be made to ensure consistency and quality of subsequent sampling. The Project Manager will have the authority to resolve any problems encountered. Assessment frequencies and responsible personnel are shown in the following table.

**Table 10: Project Assessment Table**

Assessment Type	Frequency (Annual Basis)	Person Responsible for Performing Assessment	Person Responsible for Responding to Assessment Findings	Person Responsible for Monitoring Effectiveness of Corrective Actions
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Assessment Type	Frequency (Annual Basis)	Person Responsible for Performing Assessment	Person Responsible for Responding to Assessment Findings	Person Responsible for Monitoring Effectiveness of Corrective Actions
Field sampling audit	Once after first sampling day	Field Operations Manager	Field Operations Manager	Field Operations Manager
Field analytical audit	Once after first sampling day	Project Manager	Project Manager	Project Manager
UNH laboratory audit	Quarterly (see Section VIII of Appendix A)	Laboratory Manager	Laboratory Manager	Laboratory Manager
Data Quality Audit	Annually	Project QA Officer	Project QA Officer	Project QA Officer

## C2 – Reports to Management

The Project QA Officer and/or Program Manager will produce an annual report to PREP. The final work product will be a table containing quality assured laboratory results for each station on each date and an annual report describing any deviations from the protocols established in the QA Project Plan. Data from the annual reports will be published in PREP’s State of Our Estuaries Reports.

## D1 – Data Review, Verification and Validation

The Project QA Officer will be responsible for a memorandum to PREP summarizing any deviations from the procedures in the QA Project Plan and the results of the QA/QC tests. The Project QA Officer will review all field data sheets and/or final computer data files for completeness and quality based on the criteria described in Section A7. The Project QA Officer will also *affirmatively* verify that the methods used for the study followed the procedures outlined in this QA Project Plan. If questionable entries or data are encountered during the review process (see methods in Section B5), the Project QA Officer will contact the appropriate personnel to determine their validity.

## D2 – Verification and Validation Procedures

The Project Manager will review the memorandum from the Project QA Officer to see if there have been deviations from the QA Project Plan. Any decisions made regarding the usability of the data will be left to the Project Manager; however the Project Manager may consult with project personnel or with personnel from EPA-NE, if necessary.

## D3 – Reconciliation with User Requirements

The Project Manager will be responsible for reconciling the results from this study with the ultimate use of the data. Results that are qualified by the Project QA Officer may still be used if the limitations of the data are clearly reported to decision-makers. Data for this project are being collected as part of a long-term monitoring program. It is not possible to repeat sampling events without disrupting the time series. Therefore, the Project Manager will:

1. Review data with respect to sampling design.
2. Review the QA memorandum from the Project QA Officer.
3. If the data quality objectives from Section A7 are met, the user requirements have been met. If the data quality objectives have not been met, corrective action as discussed in D2 will be established by the Project Manager.

### **References**

- PREP. 2013. State of Our Estuaries 2013. Piscataqua Region Estuaries Partnership, University of New Hampshire, Durham, NH. Published online: [www.stateofourestuaries.org](http://www.stateofourestuaries.org).
- DES, 2008. Ambient River Monitoring of Tributaries to the Great Bay Estuary 2008 - 2012 Quality Assurance Project Plan. Approved March 20, 2008. Amended March 10, 2010.