

3-2019

Great Bay Estuary Tidal Tributary Monitoring Program (GBETTMP): Quality Assurance Project Plan 2019 - 2023

Kalle Matso

University of New Hampshire, Durham

Michelle Shattuck

University of New Hampshire, Durham

Jody Potter

University of New Hampshire, Durham

Follow this and additional works at: <https://scholars.unh.edu/prep>

Recommended Citation

Matso, Kalle; Shattuck, Michelle; and Potter, Jody, "Great Bay Estuary Tidal Tributary Monitoring Program (GBETTMP): Quality Assurance Project Plan 2019 - 2023" (2019). *PREP Reports & Publications*. 418.

<https://scholars.unh.edu/prep/418>

This Report is brought to you for free and open access by the Institute for the Study of Earth, Oceans, and Space (EOS) at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in PREP Reports & Publications by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact nicole.hentz@unh.edu.

**Great Bay Estuary Tidal Tributary Monitoring Program
(GBETTMP) 2019 - 2023**

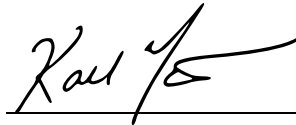
Quality Assurance Project Plan

March 2019

Prepared by

**Kalle Matso, Piscataqua Region Estuaries Partnership, University of New Hampshire
Michelle Shattuck, Water Quality Analysis Laboratory, University of New Hampshire
Jody Potter, Water Quality Analysis Laboratory, University of New Hampshire**

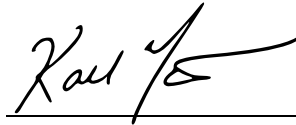
Project Manager:



March 27, 2019

Signature / Date
Kalle Matso, PREP

Project QA Officer:



March 27, 2019

Signature / Date
Kalle Matso, PREP

Laboratory Program Manager:



March 25, 2019

Signature / Date
Bill McDowell, UNH-WQAL

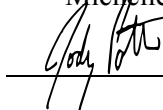
Field Operations Manager:



March 25, 2019

Signature / Date
Michelle Daley Shattuck, UNH-WQAL

Laboratory Manager:



March 25, 2019

Signature / Date
Jody Potter, UNH-WQAL

USEPA Project Officer:



April 11, 2019

Signature / Date
Erik Beck, US EPA

USEPA QA Officer:



04/03/2019

Signature / Date
Robert Reinhart, US EPA

A2 – Table of Contents

A2 – Table of Contents	2
A3 – Distribution List	3
A4 – Project/Task Organization	3
A5 – Problem Definition/Background	5
A6 – Project/Task Description	5
A7 – Quality Objectives and Criteria	6
A8 – Special Training/Certification	8
A9 – Documents and Records	8
B1 – Sampling Process Design	9
B2 – Sampling Methods	12
B3 – Sample Handling and Custody	14
B4 – Analytical Methods	14
B5 – Quality Control	15
B6/B7 – Instrument/Equipment Testing, Inspection, Maintenance, Calibration and Frequency	15
B8 – Inspection/Acceptance Requirements for Supplies and Consumables	16
B9 – Non-Direct Measurements	16
B10 – Data Management	16
C1 – Assessments and Response Actions	16
C2 – Reports to Management	17
D1 – Data Review, Verification and Validation	17
D2 – Verification and Validation Procedures	17
D3 – Reconciliation with User Requirements	17
References	18

List of Appendices

Appendix A: Quality Assurance Plan, UNH Water Quality Analysis Laboratory

Appendix B: Field Data Sheets

Appendix C: Standard Operating Procedures for Total Dissolved Nitrogen and Dissolved Organic Carbon Analyses

Appendix D: Standard Operating Procedures for Filtration for Suspended Solids Analysis

Appendix E: Standard Operating Procedures for Total Phosphorus Analyses

Appendix F: Standard Operating Procedures for Ammonia Analysis

Appendix G: Standard Operating Procedures for Nitrate+Nitrite Analysis

Appendix H: Standard Operating Procedures for Particulate Nitrogen

Appendix I: Standard Operating Procedures for Orthophosphate

Appendix J: YSI Calibration Log

List of Tables

Table 1: QAPP Distribution List	3
Table 2: Project Schedule Timeline	5
Table 3: Measurement Performance Criteria for Laboratory Samples	6
Table 4: Special Personnel Training Requirements	8
Table 5: Sample Summary	9
Table 6: Tributary Sample Locations	10
Table 7: Sampling Schedule for 2018	10
Table 8: Sample Requirements	13
Table 9: Surface Water Target Analytes and Reference Limits	14
Table 10: Project Assessment Table	17

List of Figures

Figure 1: Project Organization	4
Figure 2: Sampling locations in the Great Bay Estuary Watershed, Coastal Basin	11

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
Rachel Rouillard	PREP Director	PREP	603-862-3948 rachel.rouillard@unh.edu
Kalle Matso	Project Manager/ & Project QA Officer	PREP	603-781-6591 kalle.matso@unh.edu
Bill McDowell	Laboratory Program Manager	UNH	603-862-2249 Bill.McDowell@unh.edu
Jody Potter	Laboratory Manager	UNH	603-862-2341 Jody.Potter@unh.edu
Michelle Shattuck	Field Operations Manager	UNH	603-862-2341 Michelle.shattuck@unh.edu
Ted Diers	Data User	NH DES	603-271-3289; ted.diers@des.nh.gov
Erik Beck	EPA Project Officer	USEPA	617-918-1606 Beck.erik@epa.gov
Robert Reinhart	EPA QA Officer	USEPA	617-918-8633; Reinhart.Robert@epa.gov

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. 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 (Kalle Matso) will be responsible for coordinating all program activities.

The Field Operations Manager (Michelle Shattuck) 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.

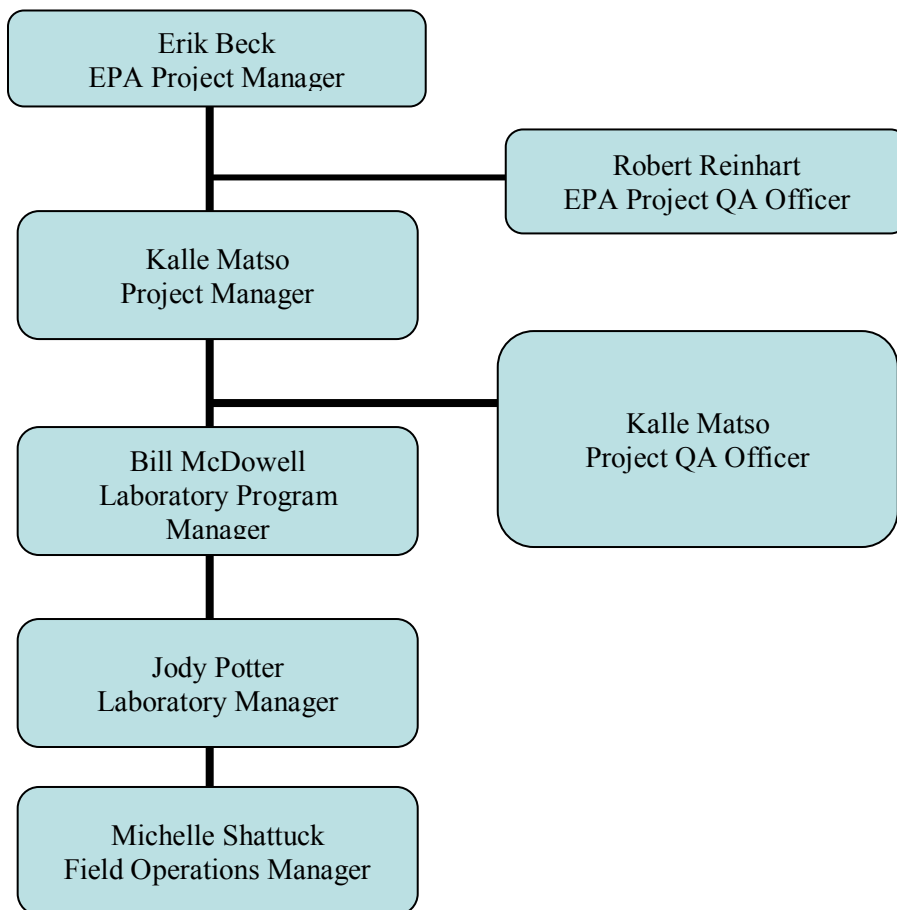
At the end of the project, the Project QA Officer (Kalle Matso) will review the results of QA/QC checks and verify that the procedures of this QA Project Plan were completed. The Project QA Officer will be responsible for a memorandum summarizing any deviations from the procedures in the QA Project Plan, 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 (Erik Beck) and the EPA Project QA Officer (Robert Reinhart). The EPA Project Manager and EPA Project QA Officer will be responsible for approving the Quality Assurance Project Plan.

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 at the end of the project with all the data and the QA summary report.

Figure 1 shows an organizational chart for this project.

Figure 1: Project Organization



A5 – Problem Definition/Background

Nitrogen enrichment continues to be a concern for the Great Bay Estuary. In the 2018 State of Our Estuaries report (PREP, 2017), 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 for the years 2019 - 2023. Nitrate+nitrite (NO₂/NO₃), ammonium (NH₄), total dissolved nitrogen (TDN), particulate nitrogen (PN), total phosphorus (TP), dissolved organic carbon (DOC), orthophosphate (PO₄) and total suspended solids (TSS) will be measured in the water samples and calculated measures include total nitrogen (TN; sum of TDN and PN) and dissolved organic nitrogen (DON; difference between TDN and sum of NO₂/NO₃ and NH₄).

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 2018. One significant change to that design was made in 2013 to TN analysis, which was changed from direct measurement of TN by the persulfate digestion method to the calculated method as suggested by USGS (Office of Water Quality Technical Memorandum 2013.01) and verified by split samples in this study for 2 years. The Sampling design is described in Section B of this QAPP. 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.

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 QAPP will apply to the years 2019 through 2023.

A6 – Project/Task Description

The tasks and annual schedule for the project are summarized in Table 2.

Table 2: Project Schedule Timeline

Activity	Dates		Product	Due Date
	Anticipated Date(s) of Initiation	Anticipated Date(s) of Completion		
QAPP/QAPP updates preparation	1/1 of sampling year	2/15 of sampling year	QAPP Document	2/15 of sampling year
Training	2 nd week of March of sampling year	3/15 of sampling year	Field crews trained on SOPs	3/15 of sampling year
Sample collection	4 th Thursday of March	3 rd Wednesday of December	Nutrient samples collected, delivered to laboratory, and stored	3 rd Wednesday of December of sampling year

Activity	Dates		Product	Due Date
	Anticipated Date(s) of Initiation	Anticipated Date(s) of Completion		
Sample analysis	Directly after sampling begins (see above)	2/1 of year following sampling year	Laboratory analyses for nutrient samples completed	2/1 of year following sampling year
Laboratory Report	1/1 of year following year of sampling	3/1 of year following year of sampling	Report from the Laboratory Manager with the final, quality-assured results for tributary samples and QC samples	3/1 of year following year of sampling
Data Quality Audit & Memo	3/1 of year following year of sampling	4/1 of year following year of sampling	Memo from QA Project Officer summarizing results of QC samples and QAPP nonconformances	4/1 of year following year of sampling

A7 – Quality Objectives and Criteria

Table 3 summarizes the performance criteria for the NO₂/NO₃, NH₄, TDN, PN, TP, DOC, PO₄ 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 < 20%	Field Duplicates
Precision-Lab	RPD < 15%	Lab Duplicates
Accuracy/Bias	>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 method detectable limit (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 20% will be marked invalid, unless the average of the two samples is less than 5X the MDL. 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 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.

Percent recovery (R) for certified reference materials will be calculated using the following equation:

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

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):

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

Representativeness: The samples will be taken at the same locations and using the same methods as used for the GBETTMP sampling in 2013-2018 if possible. (Samples collected prior to July 2016 have been moved to station 09-EXT-DAMMED in NHDES' Environmental Monitoring Database (EMD), to differentiate between samples that represent the impounded conditions verses those of the free-flowing river following the dam removal.) 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.

Sensitivity: The laboratory methods used should be capable of detecting NO₂/NO₃, NH₄, TDN, PON, TN, TP, and TSS concentrations in ambient river water. Results greater than the MDL but less than the quantitation limit (QL) will be noted as "estimated values" but will not be invalidated. Results below

the MDL will be flagged as “non-detect.” The MDL will be established using data collected in 2019 and articulated in an addendum to this QAPP, filed before 2020, when QA/QC activities will begin (EPA 2016). The UNH Water Quality Analysis Laboratory as established that the QL will equal the MDL multiplied by 3 (van Buuren 2017).

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 (scholars.unh.edu/prep).

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 QA Officer will be electronic laboratory and field 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.

Archiving

The QA Project Plan and memo will be kept on file at PREP 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 (NO₂/NO₃), ammonium (NH₄), total dissolved nitrogen (TDN), particulate nitrogen (PN), total phosphorus (TP), dissolved organic carbon (DOC), orthophosphate (PO₄), 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 NO₂/NO₃, NH₄, TDN, PN, TN, TP, DOC and TSS. Water temperature, dissolved oxygen, pH and specific conductance will be measured for information only (i.e., not reported per se but may be used for research publications, etc.)

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 schedule as well as station for the field duplicate sample are shown in

Table 7.

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 ₂ /NO ₃	8	1	10	10	90
NH ₄	8	1	10	10	90
TDN	8	1	10	10	90
PN	8	1	10	10	90
TP	8	1	10	10	90
DOC	8	1	10	10	90
PO ₄	8	1	10	10	90
TSS	8	1	10	10	90
Water Temperature	8	1	10	10*	0 (field measure)
Dissolved Oxygen Concentration	8	1	10	10*	0 (field measure)
Dissolved Oxygen Saturation	8	1	10	10*	0 (field measure)
pH	8	1	10	10*	0 (field measure)
Specific Conductance	8	1	10	10*	0 (field measure)

* See page 12 for description of how duplicate samples are achieved for parameters obtained with probes.

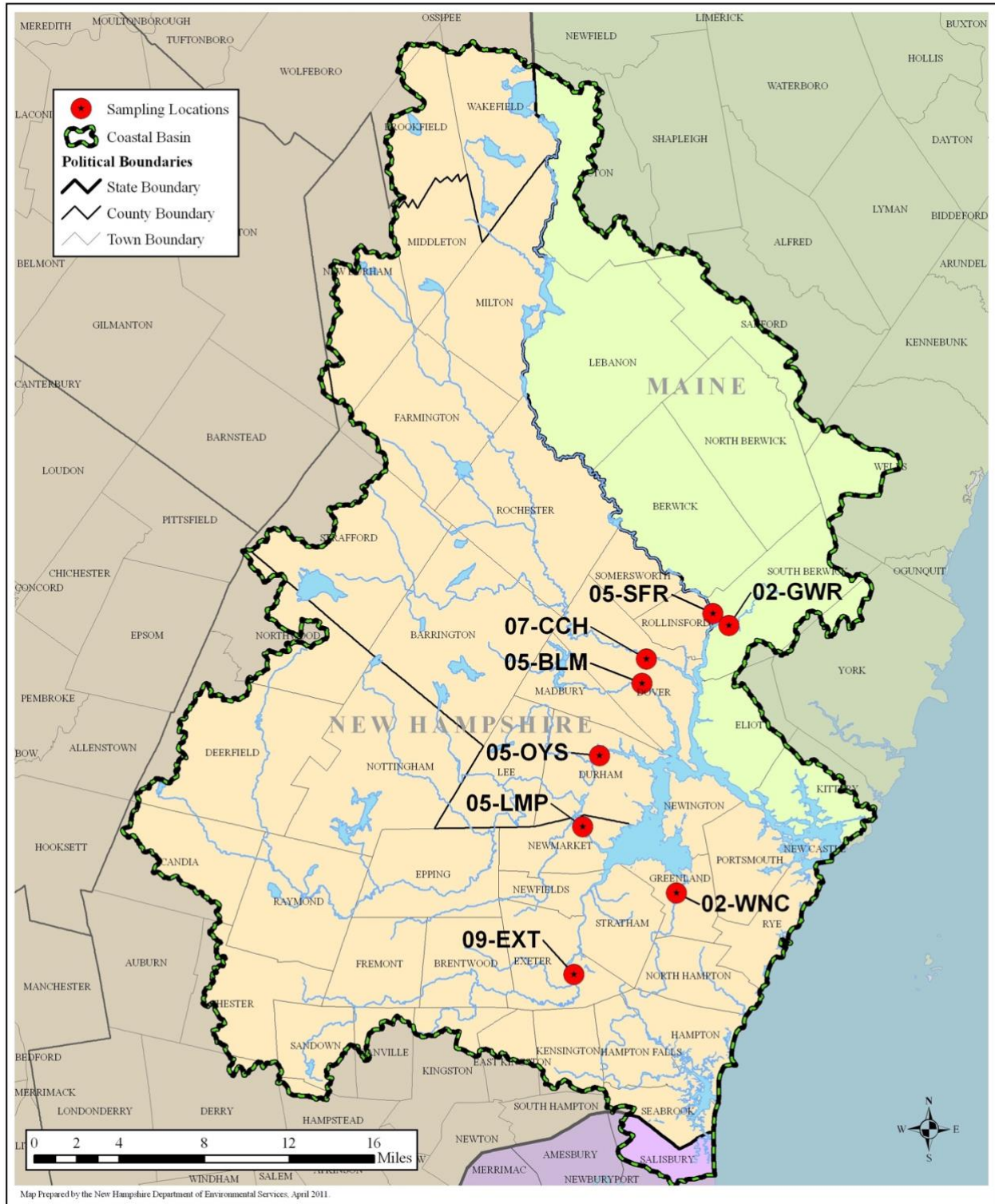
Table 6: Tributary Sample Locations

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 Cochecho	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: Targeted annual sampling schedule (with adjustments made in advance for holiday conflicts)

Month	Day of Week	Station for Duplicate Sample
March	4 th Wednesday	02-GWR
April	4 th Wednesday	02-WNC
May	4 th Wednesday	09-EXT
June	4 th Wednesday	05-LMP
July	4 th Wednesday	05-OYS
August	4 th Wednesday	07-CCH
September	4 th Wednesday	05-BLM
October	4 th Wednesday	05-SFR
November	4 th Wednesday	05-LMP
December	4 th Wednesday	05-OYS

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 because the extra volume is required to get enough particulates for analysis. 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. A calibration check is run on the YSI multiparameter meter previous to going out to the field.
2. Samples are labelled with the Station ID (Table 6), collection date, and UND ID (assigned by the lab). Field duplicates are labelled with "DUP" on the bottle. Labels are created before going out into the field.
3. On site, 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.
4. 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) after rinsing the bottle. The bucket should be shaken to fully mix the water before the water is poured off into the sample bottle.
5. If a field duplicate sample is needed at the station, the bucket will be emptied and then refilled from the river following Step 1 and all subsequent steps. Probe measurements are taken a second time when the bucket is re-filled in order to duplicate measurements for probe parameters.
6. The sample bottle(s) will be placed in a cooler with ice for transport to the laboratory.
7. The bucket will be emptied and then refilled from the river following Step 1 for field parameter measurements.
8. 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.
9. 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.
10. The chain-of-custody (COC) is filled out at each station and brought back to the lab. The field data is entered into the lab's logbook and then the COC is filed in the lab manager's office. At the end of the year the COC's are scanned into a PDF and included with the data report from the lab.

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.

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 ₂ /NO ₃	Grab	Section B2	10 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
NH ₄	Grab	Section B2	10 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
TDN	Grab	Section B2	20 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
DOC	Grab	Section B2	20 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
PO ₄	Grab	Section B2	10 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
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

*One 60 ml filtered sample bottle satisfies the above requirements with the exception of TP, which accounts for the other 60 ml bottle; however, this bottle is unfiltered.

** One dried filter satisfies the requirements for both TSS and PN.

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 organic carbon and 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 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, F, G, and H. Appendix C contains the SOP for DOC and TDN concentrations. Appendix D contains the protocol for filtering samples for total suspended solids. Appendix E contains the protocol for TP using alkaline persulfate digestion. Appendix F contains the SOP for ammonium concentrations. Appendix G contains the SOP for NO₂/NO₃ concentrations. Appendix H contains the protocol for PN using the EPA method. Appendix I contains the SOP for orthophosphate concentrations.

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	Quantitation Limit**
NO ₂ /NO ₃	USEPA 353.2 Revision 2.0, August, 1993 (App. G)	NA-data will be used for trend analysis	0.005 mg N/L	TBD

Analyte	Analytical method (See Appendices for SOP details)	Project Action Level	Analytical/Achievable Method Detection Limit	Quantitation Limit**
NH ₄	USEPA method 350.1, 1971, modified March 1983 (App. F)	NA-data will be used for trend analysis	0.005 mg N/L	TBD
TDN	High temperature catalytic oxidation (App. C)	NA-data will be used for trend analysis	0.05 mg/L	TBD
PN	USEPA Method 440.0 (App. H)	NA-data will be used for trend analysis	0.01 mg/L	TBD
DOC	USEPA Method 415.3 (App. C)	NA-data will be used for trend analysis	0.1 mg/L	TBD
PO ₄	USEPA Method 365.3 (App. I)	NA-data will be used for trend analysis	0.001 mg P/L	TBD
TN - calculated	Calculated (TDN + PN)	NA-data will be used for trend analysis	0.05 mg/L*	TBD
DON	Calculated (TDN - DIN)	NA-data will be used for trend analysis	0.05 mg/L*	TBD
TP	USGS Method I-4650-03 Alkaline persulfate digestion (App. E)	NA-data will be used for trend analysis	0.007 mg/L	TBD
TSS	APHA Method 2540-D (App. D)	NA-data will be used for trend analysis	1 mg/L	TBD

*TDN limits are used, because TN is a calculated value.

** See “Sensitivity” discussion, Page 7.

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 by printing the entire data set against the entries in each field or laboratory data sheet by the Laboratory Manager. The Project QA Officer/Project Manager 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 observations will be recorded on standard field data sheets. Data from the sensors is exported as an electronic comma-separated value (CSV) file. All laboratory data will be stored electronically and then transferred to the Project QA Officer as part of the laboratory report. The Project QA Officer 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 QA Officer, 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
Field sampling audit	Once after first sampling day	Field Operations Manager	Field Operations Manager	Field Operations 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 will be responsible for uploading a QA/QC memorandum to the PREP website (scholars.unh.edu/prep). The memorandum will include the data uploaded to the Environmental Monitoring Database as well as quality assured results of the laboratory analyses for each station on each date and a description of any deviations from the protocols established in the QA Project Plan.

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 compare the QA memorandum against 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, 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 through the QA process 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. Compare the QA memorandum with the QA Project Plan.

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

- EPA. 2016. Definition and procedure for determination of the method detection limit, Revision 2. EPA 821-R-16-006. https://www.epa.gov/sites/production/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf
- New Hampshire Department of Environmental Services. 2013. Great Bay Estuary Tidal Tributary Monitoring Program (GBETTMP) 2013-2017 Quality Assurance Project Plan. *Quality Assurance Project Plans*. 1. <https://scholars.unh.edu/qapp/1>
- PREP. 2017. State of Our Estuaries 2018. Piscataqua Region Estuaries Partnership, University of New Hampshire, Durham, NH. Published online: www.stateofourestuaries.org.
- USGS. 2013. Office of Water Quality Technical Memorandum 2013.01 Guidance on Methods for Determining the Concentration of Total Nitrogen in Whole-Water Samples. <https://water.usgs.gov/admin/memo/QW/qw2013.01.pdf>
- van Buuren BH (2017) Introduction to reporting limits. Presentation to National Water Quality Monitoring Council. https://acwi.gov/monitoring/webinars/mpsl_qa_services_intro_rls_012517.pdf

Appendix A

QAPP for the Water Quality Analysis Lab at the University of New Hampshire, Department of Natural Resources, Durham, NH

Prepared by: Jeff Merriam
Date of Last Revision: 1/10/2018
Revised by: Jody Potter

I. Laboratory Organization and Responsibility

Dr. William H. McDowell - Director

Jody Potter – Lab Manager/QA manager. Mr. Potter supervises all activities in the lab. His responsibilities include data processing and review (QA review), database management, protocol development and upkeep, training of new users, instrument maintenance and repair, and sample analysis.

Katie Swan, James Casey, & Lisle Snyder – Lab Technicians. Ms Swan, Mr Casey, and Mr Snyder’s responsibilities, with the help of undergraduate employees, include sample analysis, logging of incoming samples, sample preparation (filtering when appropriate), daily instrument inspection and minor maintenance.

All analyses are completed by Katie Swan, Lisle Snyder, James Casey or Jody Potter, and all data from each sample analysis batch (generally 40-55 samples) is reviewed by Jody Potter for QC compliance. All users are trained by the lab manager and must demonstrate (through close supervision and inspection) proficiency with the analytical instrumentation used and required laboratory procedures.

II. Standard Operating Procedures

Standard Operating Procedures for all instruments and methods are kept in a 3-ring binder in the laboratory, and are stored electronically on the Lab manager's computer. The electronic versions are password protected. SOPs are reviewed annually, or as changes are required due to new instrumentation or method development.

III. Field Sampling Protocols

Sample collection procedures are generally left up to the sample originators, however we recommend the guidelines described below, and provide our field filtering protocol on request.

All samples are filtered in the field through 0.7 um precombusted (5+ hours at 450 C) glass fiber filters (e.g. Whatman GF/F). Samples are collected in acid-washed 60-mL HDPE bottles. We prefer plastic to glass as our preservative technique is to freeze. Sample containers are rinsed 3 times with filtered sample, and the bottle is filled with filtered sample. Samples are stored in the dark and as cool as possible until they can be frozen. Samples must be frozen or refrigerated (SiO₂) within 8 hours of sample collection. Once frozen, samples can be stored indefinitely (Avanzino and Kennedy, 1993), although they are typically analyzed within a few months.

After collection and freezing, samples are either hand delivered to the lab, or are shipped via an over-night carrier. Samples arriving in the lab are inspected for frozen contents, broken caps, cracked bottles, illegible labels, etc. Any pertinent information is entered into a password protected database (MS Access).

We provide an electronic sample submission form that also serves as a chain of custody form. Submitters should indicate all analyses required for the samples,

preservation (if any), and sample information (name, date, etc ...). They should also indicate project name and a description of the project.

IV. Laboratory Sample Handling Procedures

Samples are given a unique 5-digit code. This code and sample information including name, collection date, time (if applicable), project name, collector, logger, the date received at the WQAL, sample type (e.g. groundwater, surface water, soil solution) and any other miscellaneous information, are entered into a password protected database. From this point through the completion of all analyses, we use the log number to track samples. Log numbers are used on sample run queues, spreadsheets, and when importing concentrations and run information into the database

After samples are logged into the WQAL, they are stored frozen in dedicated sample walk-in freezer or refrigerator located next to the lab. These units log temperature and alarms indicate when they are out of range. The paper print-outs are replaced quarterly and kept on file. Samples from different projects are kept separated in cardboard box-tops, or in plastic bags. Samples that may pose a contamination threat (based on the source or presumed concentration range) are further isolated by multiple plastic bags, or isolation in separate freezer space. This is typically not an issue as we primarily deal with uncontaminated samples.

We do not pay special attention to holding time of samples, as frozen samples are stable indefinitely (Avanzino and Kennedy, 1993). However, we do keep track of the date samples arrive at the WQAL, and can report holding times if necessary. After samples are analyzed they are returned to the project's manager for safe keeping or they

are held for a period of time at the WQAL to allow necessary review and analysis of the data by the interested parties (not from a laboratory QC sense, but from a project specific viewpoint). Once the data is analyzed by the project's manager(s), the samples are returned or disposed of, based on the preference of the project's manager.

Samples that arrive unfrozen, with cracked bottles/caps, or with loose caps, are noted in the database and are not analyzed. These samples are disposed of to prevent accidental analysis. The sample originator is notified (generally via e-mail) of which samples were removed from the sample analysis stream. Similarly, if while in the possession of the WQAL, a sample bottle is broken or improperly stored (e.g. not frozen), the sample is removed and the sample originator is notified.

V. Calibration procedures for chemistry

Calibration curves are generally linear, and are made up of 4-7 points. A full calibration is performed at the beginning of each run (a run is generally 40-60 samples) with a reduced calibration (3-5 points) performed at the end of the run. Occasionally calibration data is best fit with a quadratic equation, and this is used if it best describes the data within a specific run.

Standards are made from reagent grade chemicals (typically Fisher Scientific or ACROS) that have been dried and are stored in a dessicator when required. Working stock solutions are labeled with the content description, concentration, initials of the maker, and the date the stock solution was made. Generally stock solutions are kept less than one week; however some stocks (Br, Na, Cl, C for DOC) can be stored for several

months. Standard solutions are kept for less than one week from the date they were made. Stocks and standards are stored tightly covered, in a dark refrigerator in the lab.

Control charts are prepared and evaluated by the lab manager frequently.

However data from each run are looked at within days of analyses. Calibration curves, Laboratory Duplicates, Lab Fortified Blanks (LFB), Lab Fortified Sample Matrices (LFM) and Lab Reagent Blanks (LRB) are reviewed and are checked against known concentrations (where applicable) to ensure QC criteria are met for each run of samples.

VI. Data Reduction, validation, reporting and verification

Data reduction and validation are performed in a spreadsheet (MS Excel). The Raw data page of the spreadsheet lists the date of analysis, user, analysis performed, project, any issues or problems noted with the instrument on that date, and the sample queue and the raw data exported from the instruments. Most raw data is exported as an area or an absorbance value. This data is entered into an Excel QC template to guide the user on how to calculate data and QC summary. A second page (typically named “Calculations”) is added to the spreadsheet where known concentrations of standards, check standards and reference solutions are added. The calibration curve(s) is calculated and the concentrations are calculated on this page. Calculated concentrations for all standards, LFB, LFM and IPC are compared to the “known” or prepared values. If these are acceptably close ($\pm 10\%$ of the “known”) no further changes to the calculated concentrations are made. If there is evidence of drift in the response of the instrument during a run, we try to correct for the drift using the responses from the front end calibration curve and the set of standards analyzed at the end of the run. All reference

solutions and replicates must meet certain QC criteria (described below) for a run to be accepted.

Data are then exported to the WQAL database. Exported information includes the unique 5-digit code, calculated concentration, the analysis date, the user, the filename the raw data and calculations are saved in, and any notes from the run regarding the specific sample. Data are sent to sample originators upon completion of all requested sample analyses and following review by the WQAL lab manager. Generally the data include the 5-digit code, the sample name, collection date, and concentrations, in row-column format. Any information entered into the database can be included upon request. Data transfer is typically via e-mail or electronic medium (CD or floppy disk).

All data corrections are handled by the lab manager. Corrections to data already entered into the database are very infrequent. Typically they involve reanalysis of a sample. In this case, the old data is deleted from the database, and the new value is imported, along with a note indicating that it was re-analyzed, the dates of initial and secondary analysis and the reason for the correction.

Hand written or computer printed run sheets are saved for each run and filed, based on the project and the analysis. Spreadsheet files with raw data and calculations are stored electronically by analysis and date. Information in the database allows easy cross-reference and access from individual samples to the raw data and the runsheets. This provides a complete data trail from sample log-in to completion of analysis.

VII. Quality Control

All analyses conducted at the WQAL follow approved or widely accepted methods (Table 1).

Quality Control Samples (QCS) (from Ultra Scientific or SPEC Certiprep) are analyzed periodically (approximately every 10-15 samples) in each sample analysis batch to assure accuracy. The response/unit concentration is also used to monitor day-to-day variation in instrument performance. A difference 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 re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Table 2 lists historical average % recoveries. At least 2 QCS are analyzed on each run.

Standards and reagents are prepared from reagent grade chemicals (typically JT Baker) or from pre-made stock solutions. All glassware is acid washed (10% HCl) and rinsed 6 times with ultra pure-low DOC water (18.2 mega-ohm). All analyses (except CHN) use multi-point calibration curves (4-7) points, which are analyzed at the beginning and the end of each run. A Laboratory Reagent Blank (LRB), Laboratory Fortified Blank (LFB) (a standard run as a sample) and Laboratory Duplicate are analyzed every 10 to 15 samples during each run. At least one Laboratory Fortified Sample Matrix (LFM) is analyzed during each run to insure that sample matrices do not affect method analysis efficiency. Field Duplicates are not required by our lab, and are the responsibility of the specific project's manager.

Laboratory Duplicates must fall within 10% relative percent difference ($RPD = \frac{\text{abs}(\text{dup1}-\text{dup2})}{\text{average of dup1 and dup 2}}$). A difference greater than 5% requires

further investigation of the sample run. A difference greater than 10% is failure (unless the average of the two samples is less than 10X the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Long-term averages for relative % difference are included in Table 2.

LFM must show 85% to 115% recovery. A recovery <90% or > 110% requires further investigation of the sample run. A recovery <85% or >115% is failure (unless the sample is less than 10X the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Long-term averages for % recovery are included in Table 2.

All QC information from each run is stored in a separate Access database. This includes calibration r^2 , error, slope and intercept. The prepared concentration and measured concentration of LFM and calibration standards analyzed throughout the run are also entered. Finally, the lab duplicate measured concentrations are included. All this information can be queried for the project manager. Control charts (PDF) are generated from this database in R and reviewed weekly by the lab manager.

Method Detection Limits are calculated regularly, and whenever major changes to instrumentation or methods occur. Table 2 lists most recently measured MDL values.

VIII. Schedule of Internal/External Audits

Internal audits are not routinely performed, however, QC for each run is thoroughly reviewed by the lab manager before entering data into the database and a review of QC charts, and tables is done at least annually by the lab manager.

External audit samples are analyzed routinely throughout the year. The WQAL takes part in the USGS Round Robin inter-laboratory comparison study twice per year and the Environment Canada Proficiency Testing Program three times per year. The USGS and Environment Canada provide Standard Reference Samples and provide compliance results after analytical testing at the WQAL. Environment Canada is accredited by the American Association for Laboratory Accreditation. These audits are designed to quantify and improve the lab's performance. Poor results are identified and backtracked through the lab to the sources of the issue.

IX. Preventive maintenance procedures and schedules

The laboratory manager, Jody Potter, has 15 years of experience and is highly experienced with all laboratory equipment used within the WQAL. The laboratory manager conducts all maintenance and inspection of equipment based on manufacturer requirements and specifications.

Each day an instrument is used, it receives a general inspection for obvious problems (e.g. worn tubing, syringe plunger tips, leaks). The instruments are used frequently and data is inspected within a few days of sample analysis. This allows instrument (or user) malfunctions to be caught quickly, and corrected as needed.

Each day's run is recorded in the instrument's run log, with the date, the user, the number of injections (standards, samples, and QC samples), the project, and other notes of interests. Maintenance, routine or otherwise, is recorded in the instrument run log, and includes the date, the person doing the maintenance, what was fixed, and any other notes of interest.

X. Corrective Action Contingencies

Jody Potter is responsible for all QC checks and performs or supervises all maintenance and troubleshooting. When unacceptable results are obtained (based on within sample analysis batch QC checks) the data from the run are NOT imported into the database. The cause of the problem is determined and corrected, and the samples are re-analyzed. Problems are recorded in the sample queue's data spreadsheet, or on the handwritten runsheet associated with the run. Corrective actions (instrument maintenance and troubleshooting) are documented in each instrument's run log.

XI. Record Keeping Procedures

Protocols, Instrument Logs, QC charts, databases and all raw data files are kept on the lab manager's computer. These are backed up continuously, with the back up stored off site. The computer is password protected, and is only used by the lab manager. Protocols and the sample database are also password protected. Handwritten run sheets are stored in a filing cabinet in the lab. Instrument run and maintenance logs are combined with the QC data in an access database where instrument performance can easily be compared to instrument repair and the number of analyses, etc. This file is also stored on the lab manager's computer and is password protected.

All information pertinent to a sample is stored in the sample database. From this database we can easily determine the date of analysis and the location of the raw data file if further review is necessary. The amount of information provided to sample originators is dependent on what is required by the project or funding agencies.

Table 1. List of standard operating procedures and description of analyses done at the Water Quality Analysis Laboratory.

Standard Operating Procedure	Analysis	Instrument Used	Description	Protocol Latest Revision	EPA method or other reference
Ion Chromatography Protocol for Anions and Cations Protocol	Anions and Cations	Dionex ICS-1000; IonPac AS22 column Dionex ICS-1000 and ICS 1100; IonPac CS12 column	Anions via ion chromatography w/ suppressed conductivity. Cations via ion chromatography w/ suppressed conductivity	February 7, 2012	Anions EPA #300.0 Cations ASTN D6919-09
Dissolved Organic Carbon Protocol	DOC	Shimadzu TOC-V or TOC-L	High Temperature Catalytic Oxidation (HTCO)	April 4, 2016	EPA 415.3
Total Dissolved Nitrogen Protocol	TDN	Shimadzu TOC-V or TOC-L with TN module	HTCO with chemiluminescent N detection	April 4, 2016	Merriam et al, 1996; ASTM D5176
DOC and TDN combined Protocol	DOC and TDN	Shimadzu TOC-V or TOC-L with TN nitrogen module	HTCO with chemiluminescent N detection	April 4, 2016	EPA 415.3 and Merriam et al, 1996
Seal AQ2 discrete colorimetric analysis Protocol	Nitrate/Nitrite colorimetric (NO ₃ /NO ₂)	Seal Analytical AQ2 discrete analyzer	Automated Cd-Cu reduction	April 25, 2016	EPA 353.2
SmartChem discrete colorimetric analysis Protocol	Ammonium colorimetric (NH ₄)	SmartChem discrete analyzer	Automated Phenate	August 27, 2010	EPA 350.1
Seal AQ2 discrete	Soluble reactive	Seal Analytical	Automated Ascorbic acid	April 20, 2017	EPA 365.3

colorimetric analysis Protocol	Phosphorous colorimetric (SRP or PO ₄)	AQ2 discrete analyzer			
SmartChem discrete colorimetric analysis Protocol	Silica (SiO ₂)	SmartChem discrete analyzer		November, 10, 2005	EPA 370.1
Seal AQ2 discrete colorimetric analysis Protocol	Total Dissolved Phosphorus (TDP) (Filtered sample)	Seal Analytical AQ2 discrete analyzer	Persulfate Oxidation of filtered sample, followed by colorimetric SRP analysis.	April 25, 2016	USGS Test Method 1-4560-03
Seal AQ2 discrete colorimetric analysis Protocol	Total Phosphorus (TP) and Total Nitrogen (TN) (Unfiltered sample)	Seal Analytical AQ2 discrete analyzer	Persulfate Oxidation of unfiltered sample, followed by colorimetric SRP analysis.	April 25, 2016	Resources Investigations Report 03-4174
CHN Protocol	Particulate Carbon (PC) and Nitrogen (PN)	Perkin Elmer 2400 Series II CHN	Filtration of sample followed by Elemental Analysis of the filter and particulates	February 14, 2013	EPA 440.0
Particulate Carbon and Nitrogen filtration	Laboratory Sample Filtration		Filtration of samples for water chemical analysis and particulate analysis	February 14, 2013	EPA 440.0
Acid Washing Protocol	Glass and plastic-ware cleaning		10% HCl rinse and 6 rinses with DDW	July 19, 2012	
Field Filtering Protocol	Sample prep		3-times rinse with filtered sample	July 13, 2015	
Fluorescence	EEMs	Horiba Jobin Yvon Fluoromax 3	Scanning Fluorescence Excitation & Emission on whole water	June 26, 2013	
Absorbance	Abs 254 & SUVA	Shimadzu TOC-V & Shimadzu	Scanning absorbance	June 26, 2013	EPA 415.3

		PDA SPD-M20A	spectra on whole water		
pH, Closed cell	pH, Closed cell	Electrode & Thermo Orion 525A	pH in a closed environment under atmospheric CO2 conditions	August 27, 2015	EPA 150.1
pH, aerated	pH, aerated	Electrode and Radiometer ION450	pH equilibrated with atmosphere	January 4, 2013	EPA 150.1
Specific conductance	Specific conductance	Electrode	Specific conductance	May 15, 2017	EPA 120.1
ANC protocol	ANC	Electrode & Radiometer ION450	Gran titration	May 15, 2017	EPA 310.1
Greenhouse Gases	Greenhouse Gases extracted from water	Shimadzu GC-2014	CH4, N2O, & CO2 on GC with FID, ECD, & TCD	December 6, 2012	
Alkalinity protocol	Alkalinity	Electrode & Radiometer ION450	Inflection Point		EPA 310.1

Table 2. Detection limits, acceptable ranges, and recent historical averages for QC samples at the Water Quality Analysis Lab.

¹ Detection limit based on user experience and previous analysis (not statistically calculated). ² Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

Analyte	Units	Typical Range	Regression Type	# of Cal. Points	MDL ²	Lab Duplicate % Relative Difference	Limit	LFM % recovery	Limit +/-	IPC % recovery	Limit +/-
SiO ₂	mg SiO ₂ /L	0 – 40	Linear	4-7	.01	3.5	15.0	92.8	15.0		
PO ₄	µg P/L	0 – 200	Linear	4-7	5	7.8	15.0	95.5	15.0	93.7	15.0
NH ₄	µg N/L	0 – 200	Linear	4-7	5	7.1	15.0	103.9	15.0	95.0	15.0
NO ₃ FIA	mg N/L	0 – 10	Linear	4-7	0.005	4.6	15.0	100.9	15.0	102.6	15.0
Na ⁺	mg Na/L	0 – 15	Quadratic	4-7	0.02	0.9	15.0			112.7	
K ⁺	mg K/L	0 – 7	Quadratic	4-7	0.02	10.4	15.0			97.8	
Mg ²⁺	mg Mg/L	0 – 7	Quadratic	4-7	0.02	4.5	15.0			89.7	
Ca ²⁺	mg Ca/L	0 – 10	Quadratic	4-7	0.1	4.0	15.0			98.2	
Cl ⁻	mg Cl/L	0 – 15	Quadratic	4-7	0.02	1.6	15.0			92.7	
NO ₃ ⁻	mg N/L	0 – 3	Quadratic	4-7	0.004	0.3	15.0			96.3	
SO ₄ ²⁻	mg S/L	0 – 8	Quadratic	4-7	0.04	2.2	15.0			86.5	
TDN	mg N/L	0 – 10	Linear	4-7	0.035	7.8	15.0	100.3	15.0	102.1	15.0
DOC	mg C/L	0 – 20	Linear	4-7	0.05	4.9	15.0	100.5	15.0	97.0	15.0

References

Avanzino R.J. and V.C. Kennedy, 1993. Long-term frozen storage of stream water samples for dissolved orthophosphate, nitrate plus nitrite, and ammonia analysis. *Water Resources Research*, 29(10) 3357-3362.

Merriam, J.L, W.H. McDowell, W.S. Currie, 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. *Soil Science Society of America Journal*, 60(4) 1050-1055.

Appendix B

New Hampshire Estuaries Project Tributary Sampling Field Data Sheet

Collected By: _____ Date/Time Samples Delivered to WQAL: _____

Specific Conductance Meter Check (500 uS/cm standard): _____ uS/cm (OK if 475 – 525 uS/cm)

Station ID	UNH ID	Sample Time	Water Temp (oC)	Conduc tance (uS/cm)	Specific Conduct ance (uS/cm at 25 °C)	pH	Dissolved Oxygen mg/L	Dissolved Oxygen %	Turbidity (FNU)	Comments
167668	05-OYS									
167669	05-LMP									
167670	09-EXT									
167671	02-WNC									
167672	02-GWR									
167673	05-SFR									
167674	07-CCH									
167675	05-BLM									
167676	09-EXT Dup									

For field duplicate samples, the StationID should be the station where the sample was collected followed by “DUP”.

If you have any questions, contact Michelle Daley at 603-862-1794 or 603-767-2757 (cell)

Appendix C

Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN) Standard Operating Procedure Shimadzu TOCL and TOCV CPH

Water Quality Analysis Laboratory at the University of New Hampshire

Prepared by: Jody Potter
Date of Last Revision: 4/12/2016

Signature of Reviewer/Reviser:

Method is based on:

EPA Method 415.1 Organic Carbon, Total (Combustion or Oxidation).

And

TDN Method: Method Reference: Shimadzu Scientific Instruments Inc., TOC-V with TNM-1 Nitrogen Module. High Temperature Catalytic Oxidation with chemiluminescent detection. Merriam, J.L., W.H. McDowell, W.S. Currie, 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. Soil Science Society of America Journal, 60(4) 1050-1055.

Protocol for TOC-V CPH and TOC-L CPH

There are one of each of these machines. The TOC-V CSH can analyze NPOC and TDN in the same run.

NPOC Method: Official Name: **EPA Method 415.1** Organic Carbon, Total (Combustion or Oxidation). Organic carbon in a sample is converted to carbon dioxide by catalytic combustion or wet chemical oxidations. The carbon dioxide formed can be measured directly by an infrared detector or converted to methane and measured by a flame ionization detector. The amount of carbon dioxide or methane is directly proportional to the concentration of carbonaceous material in the sample.

TDN Method: Method Reference: Shimadzu Scientific Instruments Inc., TOC-V with TNM-1 Nitrogen Module. High Temperature Catalytic Oxidation with chemiluminescent detection. Merriam, J.L., W.H. McDowell, W.S. Currie, 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. Soil Science Society of America Journal, 60(4) 1050-1055.

A precisely measured aliquot of filtered sample is injected and combusted on a catalyst at 720 C. All fixed N is converted to Nitric Oxide (NO) and then coupled with ozone (O₃) producing Nitrogen Dioxide* (NO₂*) which is measured chemiluminescently.

1. Preparation of Standard Solutions

- A. **NPOC.** Weigh out 2.125 g dried potassium acid phthalate (KHP). Dissolve it in 500 mL of Milli-Q water (DDW) in a 1 L volumetric flask. Bring the solution to volume. This makes a 1000 mg C L⁻¹ TC stock (1000 ppm). **TDN.** Weigh out 0.60677 g dried sodium nitrate. Dissolve it in a 100 mL volumetric flask and fill to volume. This makes a 1000 mg N L⁻¹ NO₃ stock solution.
- B. If the samples to be analyzed are at the lower end of the concentration range, it may be necessary to make an intermediate standard (100 mg L⁻¹).
- C. When doing more than one analysis, NPOC and TDN standards should be combined in the same volumetric flask to reduce the amount of standard vials taking up space on a run. The lowest NPOC standard should be combined with the lowest TDN standard and so on.
- D. Make working standards by pipetting the appropriate amount of stock (or intermediate standard) into 250 mL volumetric flasks, and bring them to volume. You can put the 250 mL volumetric flasks directly on the analytical balance, allowing you to know exactly how much stock you are adding. This eliminates the necessity of weighing water (to determine the volume dispensed) before using the adjustable pipettes.

- E. Store stock solution in clean, airtight, glass container in the refrigerator. TOC stock will keep for two (2) months. The NO₃ and IC stock will keep for about one (1) month. Working standards can be stored in the volumetric flasks that they were made in. Be sure to cover them tightly with Parafilm. An airtight seal is especially important for the IC stock and standards due to absorption of CO₂ from the atmosphere. TOC and TDN standards are good for a week or so. IC standards should be remade every 2 or 3 days. Standards should be made weekly, or more frequently if dealing with low concentrations (< 0.3 mg/L). Refer to Acid Washing protocol for details.

2. Sample Preparation

- A. Sample vials (9 mL or 22 mL) are prepared by rinsing them at least 2 times with DDW and then combusting them in the muffle furnace at 450 - 500°C for 6 hours. It takes the muffle furnace one hour to get up to temperature.
- B. Fill each vial about ½ full for 22 mL vials. Fill the 9 mL vials completely full.
- C. Cover the 22 mL vials with the caps that are provided. The septa should be removed and new ones should be put in the caps every 3-4 runs. You should be able to tell how many times the caps have been pierced. The dark side of the septa should face up.
- D. Put the vials in the sample tray. The sample tray can be removed from the autosampler by lifting the hood and releasing the magnet that holds the tray down. You can then simply lift the sample tray off the autosampler.
- E. Please refer to the **Quality Assurance and Control Section** for information on replicates, certified reference standards and check standards. A copy of the NPOC/TDN/POC runsheet is attached.

3. System Inspection

- A. Confirm gas pressure on the TOC gas generator. Carrier Flow meter (on TOC-V CSH) should read about 150 mL min⁻¹.
- B. Inspect the dehumidifier drain vessel water level. The water in the drain vessel should reach the outflow port on the drain vessel sidewall. Add DDW to get it to that level, if necessary. Make sure there is no bubbling in the drain vessel. If there is, inspect the halogen scrubber and membrane filter for plug.
- C. Inspect humidifier water level. Confirm that the water level is between the two line markings. Add DDW through the supply port if necessary.
- D. Inspect the IC reagent reservoir on outside of instrument. This reservoir should have some solution. If it is empty, you must fill it with H₃PO₄ according to recipe.
- E. Inspect needle rinse bottle to the left of the autosampler. It should be filled with DDW.
- F. Inspect the HCl bottle on the outside of the instrument. It should be filled with 2N HCl for NPOC and POC analysis.

- G. Inspect the dilution water bottle to the left of the instrument and make sure it is filled with DDW (only necessary if going to do auto dilution with the instrument).
- H. Perform a leak check. The IC vessel inside the instrument should be bubbling.

4. Preparation for Analysis

- A. Check to see that waste vessel for the TOC-V (TOC-L drains to sink) is relatively empty, and that the waste tube is in the waste vessel and has no kinks.
- B. The TOCs are normally left on. If it is off, then turn it on and allow the furnace to heat up.
- C. The system setup for the instrument is usually set to be done from the computer. Ask the lab manager for help if the instrument screen is on. **Start up the software**, which is labeled TOC Control L or V. Then click on the **Sample Table Editor** icon. It will ask you for user and password, but just click ok with nothing filled in.
- D. Open a new sample table by selecting **New** from the **File menu**. Click on the **sample run** icon and then click **OK**.
- E. To establish communication between the software and the instrument, select the **connect** icon on the toolbar. The Parameter Configuration dialog box is displayed. Click the **Use Settings on PC button** for TOC-V.
- F. Insert the samples by first placing the cursor in the first line of the sample table. From the insert menu, select **sample**. The Insert **multiple samples** for TOC-L and **Auto Generate** for TOC-V option may also be selected if you have several values of the same type (i.e. standards or samples) in a row (manual section 4.4.5.1 “Auto Generate”).

For single samples (sample):

1. Click on the **Method** radio button. Select one of the previously created method files depending on which method you need (i.e. NPOC-TN method) to perform the type of analysis you are doing. Then click **next**.
2. Type in the **name of the sample** in sample name and sample ID. Change the **number of determinations** if you want it to be sampled more than once.
3. Click on **next** until you click on **finish**.
4. Continue as needed.

For several samples in a row (Auto Generate):

1. Click on the method radio button. Select one of the previously created method files depending on which method you need (i.e. NPOC-TN method) to perform the type of analysis you are doing. Then click **next**.
2. Type in the **number of vials**, the **start vial**, and the **name of the samples**. If entering ID numbers, select **Index Start** instead of entering the name of the samples. Type in the ID number of the beginning vial for the string of samples.
3. Click **next** until reach finish and then click **finish**.

- G. **Save** the Sample Table by selecting Save from the File menu.

- H. Check the status of the instrument detectors before starting analysis. From the Instrument menu, select **Background Monitor**. On the TOC tab, the status of the baseline should be OK for each parameter (position, fluctuation, and noise). Do the same for the TN tab. Then close the window.
- I. Place the cursor in the first row of the Sample Table. From the Instrument menu, **select Start**, or click on the Start button on the toolbar. The Standby window is displayed.
- J. Press **standby**. The Sparging/Acid Addition window is displayed.
- K. Verify the vial positions, and then click **OK**.
- L. The Start ASI measurement window is displayed. Click on **Start**.

5. Data Export

- A. Click on File and select **ASCII Export options**.
- B. Click on the **data** tab and select sample ID, dilution (if needed), inj no, analysis (inj.), and mean area. Click **OK**.
- C. Click on File and select **ASCII Export**. Choose a file name and **save** it under the data directory for the TOCs. The data file is now ready to be used in Excel.

6. Quality Assurance and Control

- A. **Blank Stabilization.** At least three blanks should be run at the start of your run to allow for blank stabilization.
- B. **Standard Replicates, Sample Replicates, Certified Reference Standards**
 - 1. A blank, two standard replicates, a known stream sample (CCV) and two certified reference standards (“QC”; one for NPOC/POC and one for TDN) will be run about every 12 samples as identified on the run sheets. The date for the QC standards and CCVs should be written down on the run sheet. This will allow you to track the run to run variability of your analysis, as well as to confirm the accuracy of your standards.
 - 2. At the end of your run, a standard curve consisting of four standards and a blank will be run. This will help to detect and account for any drift in the calibration during the run.
- D. **Quality Control Table.**
 - 1. The data is to be copied and pasted into the appropriate lab Excel Report Template on the TOC-V computer and the file should be named by date of analysis (described in worksheet). This template will guide you to report the QC results for the run. This includes % recovery of QC standards (CRM), run time check standards, and lab duplicates. Lab % recovery of sample duplicates, run time check standards, and QC standards should be between 85 and 115 % (see WQAL QAPP for more information).
 - 2. When completed copy the Excel file into the lab manager’s directory on the main lab computer. This information, along with the data, will be entered into the WQAL database by the lab manager to create control charts.

Appendix D

STANDARD OPERATING PROCEDURE

for determination of

Total Solids, Total Suspended Solids

and Total Dissolved Solids

in Aquatic Systems

Water Quality Analysis Laboratory at the University of New Hampshire

Prepared by: Jody Potter

Date of Last Revision: 5/15/2018

Signature of Reviewer/Reviser:

Note: This is first step before analyzing samples for particulate Nitrogen

1.0 SCOPE AND PURPOSE

Natural waters contain varying amounts of solid materials in a wide range of sizes. "Dissolved" substances include individual molecules, ions, atoms and colloids (the smallest clay particles). "Particulates" or "suspended solids" are larger particles of mineral or organic material from large clays up to sand. Total Suspended Solids (TSS) is the mass per unit volume of solids that are retained by a 1.5 μm filter (ProWeigh cat# F93447MM).

2.0 MATERIALS AND EQUIPMENT

Equipment

Drying oven that can be set to 80, 95 and 105°C
Analytical balance (measures down to 0.0001g = 0.1 mg)
Vacuum Pump

Materials

1L graduated cylinder
membrane filters & aluminum weighing dishes (pre-weighed glass fiber filters;
47mm)
desiccator with desiccant
forceps
membrane filter funnels
1L sidearm flasks
1L polyethylene sampling bottles, labeled.

3.0 SAMPLING PROCEDURE

- Sample bottles should be made of an inert material like high-density polyethylene (HDPE), low-density polyethylene (LDPE) or polypropylene (PP). Wide-mouth bottles are essential for collecting samples for sediment analysis. All sample bottles should be 10% HCl for at least 10 minutes and rinsed four times with ultra-pure (DDIW) water. Under low flow, low suspended sediment conditions, 2L or more of sample should be collected for best accuracy.
- A duplicate sample should be analyzed with each batch of samples. Collect at least 2L of sample for this purpose (see section 7).
- The amount of sediment being measured can be minute, therefore any contamination of the interior of the bottles or caps by soil, fingerprints, or even dust can alter the test results. Keep bottles capped until you are ready to collect the sample. Replace the cap immediately after filling the sample bottle.
- Before collecting the sample, fill out the label on the bottle. Each bottle label should contain the date, sampling location, and collector's initials. In a field notebook or field data sheet, record the date, sampling location, time (24 hr), any relevant field notes (flow conditions, visible sediment etc) and collector's name.
- When collecting the water sample, try to sample as close to the middle of the stream as possible. A simple sampling pole can be constructed from a broom stick or a closet rod and an adjustable duct clamp.
- Remove the cap, submerge the bottle in the water with the bottle opening facing upstream. Make sure any part of you that is in the water is downstream from the bottle. Collect water from the upper 10 cm of the stream. If the stream is shallow, do your best to avoid stirring up sediment. Try not to get bugs, leaves, sticks, etc. in the bottle.
- Store samples in a cooler with ice until return to the laboratory. Refrigerate the samples as soon as possible to slow down decomposition of organic matter. Analyze samples within 48 hours.

4.0 SAMPLE PREPARATION

Use the pre-weighed 25mm filters. They have an ID# and weight on the aluminum holding tin. It is very important that the filter be kept in its respective pan to assure correct identification. The filters should be stored in a desiccator before measuring the pre-weights because they will collect moisture in the lab.

5.0 ANALYSIS

5.1. Filtration

- Assemble filter apparatus (vacuum pump, side arm flask and funnel base).
- Select a pre-weighed filter and tin. Record the sample id (and collection date if necessary), filter id and filter weight on the TSS data sheet.
- Using forceps, place the filter on the base of the filter tower.
- Wet the filter using a few drops of DDW to seat the filter.
- Gently place the top of the filter tower on the base, and secure as necessary.
- Shake sample bottle vigorously to suspend any sediment that has settled on the bottom and produce a homogenous solution.

- Pour sample into a large graduated cylinder (1 L) and record volume of sample on the TSS data sheet. Pour sample into filtration apparatus in small quantities (approximately 100 mL), making sure not to overflow over the top. Add sample until filtration becomes very slow. Allow last of sample to be pulled through and for the filter to dry.

- If the filtration slows down before the entire graduated cylinder has been filtered, record the actual volume filtered (volume poured into graduated cylinder minus volume remaining) and discard the remaining sample. It is important to always filter the entire sample poured into the filtration apparatus and it may be necessary to use less than 1 L of sample under elevated suspended sediment conditions (e.g. during high flow). Under low flow, low suspended sediment conditions, 2L or more of sample may be filtered to capture a significant amount of sediment on the filter. Just be certain to record actual volume filtered and to not overflow side-arm flask into vacuum pump

- Using forceps transfer the filter paper to the original pre-labeled aluminum weighing dish.

- Discard filtrate

- Rinse filter apparatus and graduated cylinder with DI.

5.2. Measuring Dry Mass

- Place aluminum dishes with filters in 105°C oven for at least 24 hours.
- Remove from oven and turn off oven
- Place in desiccator to cool before weighing. Try to limit the time the filters are out of the desiccator prior to weighing as they will absorb moisture from the air.
- Calibrate the balance (See below) and zero the balance. Be sure the balance is level by verifying that the bubble is in the center of the circle and is isolated from wind and vibrations (don't lean on the bench when while weighing). Be certain that the balance is free of any debris on or near the balance pan.
- Using forceps, place the filter on the balance. Weigh only the filter as the weight on the tin is for the filter only!
- Allow the balance to stabilize and record the mass as "**Filter post-weight**" in TSS lab datasheets .
- Record any notes, problems, or observations on the TSS data sheet.
- Put the weighed filter back into its respective pan, and put the pan/filter back into a desiccator until the data can be calculated and checked or save/prepare the filter for particulate analysis. Discard filters and tin once TSS data has been checked by lab manager.

Calibrating the balance

- Calibrate the balance daily,
- Zero the balance.
- Place the smaller of two calibration weights on the balance (use 2 weights that are appropriate for the masses you'll be measuring).
- Record the mass on the log sheet, including your initials, and the date.
- Remove the weight from the balance.
- Zero the balance.
- Place the larger of the two calibration weights on the balance.
- Record the mass on the log sheet, including you initials, and the date.

6.0 Calculations, Units and Data Recording

Total Suspended Solids

$$\text{TSS (mg L}^{-1}\text{)} = \frac{(\text{Filter Post-Weight (mg)} - \text{Filter Pre-Weight (mg)}) * 1000}{\text{Sample Volume (mL)}}$$

7.0 QUALITY ASSURANCE/QUALITY CONTROL

7.1. Precision Check (Replicates) Samples

For every 10 samples analyzed, include a **Precision Check** sample:

- a. After analyzing 10 samples, process a replicate sample. A replicate is a second subsample removed from a sample bottle and carried through the entire analysis. Record the result in the QC section of the Laboratory Bench Sheet.

7.2. Method Blanks

For every 10 samples include a **DDIW blank** sample. Filter it just as you would a normal sample. Subtract the blank value from all sample values.

7.3. Field Blanks

Twice a year, include a **field blank**. Add DDIW to a clean sampling bottle and carry it into the field during sampling. Then analyze it as if it were a sample. Record the results in the QC section of the Laboratory Notebook.

7.4. MDLs

The **Method Detection Limit (MDL)** is determined once per year by processing several low concentration samples through the complete analytical method (including filtering, storage, digestion, dilution, addition of preservatives or reagents, etc.).

- a. Collect 7 liters of river or stream water. Take seven 1000-mL subsamples from this sample and process each through the entire analysis. Calculate the standard deviation (*s*) of the 7 values. Estimate the MDL in the following manner:

$$\text{MDL for TSS (mg L}^{-1}\text{)} = t * s$$

where *t* is the *t*-value from a one-sided *t* distribution at the 99% level and 6 degrees of freedom (*t* = 3.143). Include these results in the Laboratory Notebook and report the MDL in all laboratory reports.

8.0 References

American Public Health Association. 1995. Solids:2540 *In* (A.D. Eaton, L.S. Clesceri and A.E. Greenberg, eds.) Standard Methods for the Examination of Water and Wastewater. 19th ed. APHA, Washington, DC. section 2, p. 53.

U.S. Environmental Protection Agency. 1983. Methods for Chemical Analysis of Water and Wastes. Environmental Monitoring and Support Laboratory, Cincinnati, OH. EPA-600/4-79-020.

Appendix E

Total Phosphorous (TP) Standard Operating Procedure using SEAL Analytical Discrete Multi-Chemistry Analyzer (AQ2)

Water Quality Analysis Laboratory at the University of New Hampshire

Prepared by: Katie Swan
Date of Last Revision: 1/30/2019

Signature of Reviewer/Reviser:

Method is based on:

USGS Water-Resources Investigations Report 03-4174, "Methods of Analysis by the US Geological Survey National Water Quality Laboratory-Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorous in Water."

Total P (TP), Total Dissolved P (TDP), Total N (TN) and Total Dissolved N (TDN) using Alkaline Persulfate Digestion.

Introduction

This digest is applied to water samples to convert all species of P into PO₄ and all species of N to NO₃. The resulting digestion can be measured by automated colorimetry on the SEAL AQ2 for PO₄ and NO₃ to give Total P and N, respectively. Dissolved vs Total is operationally defined as digesting a filtered sample (GF/F) or an unfiltered sample.

The method is based on USGS Water-Resources Investigations Report 03-4174, "Methods of Analysis by the US Geological Survey National Water Quality Laboratory- Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorous in Water."

Method Detection Limits (MDL) have been calculated to be 6 ug P/L and 10 ug N/L. Reporting Detection Levels (RDL) are approximately 15 ug P/L and 50 ug N/L. Precision for TP and TDP is approximately +/- 5 ug P/L or 10%, whichever is greater. Precision for TN and TDN is approximately +/- 10 ug N/L or 10%, whichever is larger.

Reagent Preparation

1.5 M Sodium Hydroxide

Dissolve 60 g Sodium Hydroxide (NaOH) in about 800 mL of DI water in a 1 L volumetric flask. Let cool and fill to volume with DI water. This should be stable for months. (12 g NaOH in 200mL DI water).

2x Recrystallized Potassium Persulfate (K₂SO₈)

Even the cleanest reagent grade Potassium Persulfate appears to be loaded with Nitrogen, so it's critical that it be purified by recrystallizing twice it prior to use.

Potassium persulfate recrystallization

1. Dissolve 100 g of potassium persulfate in approximately 600 ml of Milli-Q previously heated to 60° C. Use a medium sized stir bar and a 1000 mL flask.
2. Filter the solution rapidly through a sintered glass funnel.

3. Rinse the 1000 mL flask
4. Pour filtrate back into the flask used to heat the potassium persulfate solution.
5. Cool solution to about 4° C by placing the flask in ice water or freezer. Whirl the flask continuously to prevent the solution from freezing. (~1.5 hours in freezer)
6. Filter the 4° C solution and wash with 1 or 2 squeezes of ice cold Milli-Q, save the white solid.
7. Discard the filtrate from the sidearm flask.
8. Rinse the flask used to cool the solution with Milli-Q
9. Fill the flask with 450ml of Milli-Q and heat to 60° C.
10. Add the crystals from step 5 and mix into solution.
11. Repeat steps 4 and 5. The white granules on top of the filter are crystals!
12. Dry crystals in a vacuum desiccators. Rapid drying in a good vacuum and thus at a low temperature is essential as this will minimize the sulfuric acid formation on the crystals. Drying will be complete in several days.

Working digest solution

Add 18 grams of 2x recrystallized Potassium Persulfate and 45 mL of the 1.5 M Sodium Hydroxide solution to about 350 mL of DI. Swirl to dissolve. Once dissolved, fill to 450 mL. Prepare this daily.

Fill to	with DI	150mL	300mL	450mL
2x recrystallized Potassium Persulfate		6g	12g	18g
1.5 M Sodium Hydroxide		15mL	30mL	45mL

Standards, blanks and QC sample preparation

Blanks, standards and QC samples should all be digested using the same method as the samples. Blanks are DI water. Standards should be made from PO₄ and NO₃ stock solutions. QC samples should be one of the several Ultra Scientific QC reference samples we have in the freezer. Pick one that will be appropriate to the range of standard concentrations (typically 6-200 ug P/L or 6-500 ug N/L). Also, prepare another QC check from a Disodium EDTA stock solution (for N) and a sodium pyrophosphate stock solution (for P). Prepare extra blank digestions, as you'll need the blank as the diluent for both the PO₄ and NO₃ analyses on the Smartchem.

PREPARE...	FOR EVERY...
1 Blank (DI)	~10 samples
1 Standard (#1-6)	~25 samples
1 QC (TN/TP)	~16 samples
1 CCV (UNFILTERED)	~16 samples
1 NO ₂ QC	~32 samples
1 SAMPLE REP	~12 samples

Digestion

1. Use acidwashed 20 mL PP widemouth bottles for sample digestion.
2. Shake sample thoroughly, then pipette 10 mL of sample into the digestion bottle.
3. Add 5 mL of digestion solution.
4. A replicate digest should be done every 10-12 samples.
5. Cap loosely (threads hardly engaged) and put in autoclave for 1 hour.
Autoclave Cycle #11 Liquids. Sterilize Temp = 121°C, Pressure = 117.2 kPa
6. Let samples cool after digestion.
7. Cap tightly until analysis.

Samples are ready for analysis. They can be placed in the refrigerator until time for analysis on the SEAL AQ2 using the appropriate protocols. PO₄ based on EPA 365.1 (molybdate blue method), and NO₃ based on EPA 353.2 (Cd-Cu reduction).

Note: For TN method, use the Smartchem working buffer reagent.

Working Buffer (TN analysis) - Ammonium Chloride Buffer, pH 8.5

Concentrated hydrochloric acid (HCL)	105 mL
Ammonium hydroxide (NH ₄ OH)	95 mL
Ethylenediaminetetracetic acid disodium salt dehydrate (Disodium EDTA)	1.0 g
DI water	Dilute to 1 L

Adjust pH to 8.5 with HCL or 5 N NaOH

In a 1 L volumetric flask, add 500 mL of DI water, dissolve 1.0 g of disodium EDTA, 105 mL of concentrated hydrochloric acid, and 95 mL of ammonium hydroxide. Fill to mark with DI water and mix well. Adjust the pH to 8.5 using 5 N sodium hydroxide or HCL.

CAUTION- **Fumes** will be produced when add ammonium hydroxide to the mixed solution with HCL and disodium EDTA.

Appendix F

NH₄ Standard Operating Procedure using Smartchem Discrete Analyzer

Water Quality Analysis Laboratory at the University of New Hampshire

Prepared by: Jody Potter

Date of Last Revision: 8/27/10

Signature of Reviewer/Reviser: _____

Method is based on:

USEPA Method 350.1, 1971, modified March 1983. Determination of Ammonia Nitrogen by Semi-Automated Colorimetry.

Protocol NH₄

Introduction

The Smartchem discrete auto-analyzer performs the same analytical methods as manual colorimetric assays done on a lab bench. We analyze NO₃+NO₂, PO₄, NH₄, and SiO₂ on surface, ground, soil extracts and saline waters routinely with this instrument.

The NH₄ method is based on the USEPA method 350.1, 1971, modified March 1983. The sample is buffered at a pH of 9.5 with a borate buffer to decrease the hydrolysis of cyanates and organic nitrogen compounds, and is distilled into a solution of boric acid. Ammonia reacts with alkaline phenol and then hypochlorite to form indophenol blue. The amount of color developed is proportional to the concentration of ammonia. The color is further intensified through the addition of sodium nitroprusside and measured at 630 nm.

Preparation of Standards and Reagents

1. Prepare 1000 mg N L⁻¹ NH₄ stock by dissolving 3.819g ammonium chloride in a 1000 mL volumetric flask and fill to volume.
2. If the samples to be analyzed are at the lower end of the concentration range, it may be necessary to make an intermediate standard (100 mg N L⁻¹).
3. Make working standards by pipetting the appropriate amount of stock (or intermediate standard) into 100 mL volumetric flasks, and bring them to volume. You can put empty 100 mL volumetric flasks directly on the analytical balance, allowing you to know exactly how much stock you are adding. This eliminates the necessity of weighing water (to determine the volume dispensed) before using the adjustable pipettes. Write down how much standard was added & give to lab manager. We typically use 6 working standards ranging 0-200 µg NH₄-N/L for the NH₄ determination in surface waters.
4. Store stock solution in clean, airtight, glass container in the refrigerator. The NH₄ stock will keep for about two weeks. Working standards can be stored in the volumetric flasks that they were made in. Be sure to cover them tightly with Parafilm. Standards are good for a week or so. Standards should be made weekly, or more frequently if dealing with low concentrations (< 200 µg/L).
5. A QC standard reference sample is run along with samples in a run. They can be found in the freezer with its concentration on the bag label. Dilute as necessary to bring it within your working concentration range. Also run a Lamprey QC, which is a large batch sample from the weekly Lamprey site, as a reference. There should be a bag of them in the freezer as well.
6. Preparation of the working reagents for the method:
 - a. Sodium phenolate: Using a 100 mL volumetric flask, dissolve 3.2g NaOH in 50 mL DI water. Cool the flask containing the solution to room temperature (I

- usually put in the freezer for 10-15 minutes) and then add and dissolve 8.8 mL phenol. Keep away from light. Solution is stable for two weeks.
- b. Sodium hypochlorite solution: Prepare fresh daily. Dilute 33 mL of bleach containing 5.25% NaClO to 100 mL with DI water. Add 1.0 mL concentrated Probe Rinse Solution.
 - c. Disodium ethylenediamine-tetraacetate (EDTA): Dissolve 5g EDTA disodium salt dihydrate and 2.75 g of NaOH in approximately 75 mL DI water. Add 0.6 mL Probe Rinse solution and dilute to 100 mL.
 - d. Sodium nitroprusside: Dissolve 0.3g sodium nitroprusside dihydrate (sodium nitroferricyanide dihydrate) in 100 mL of DI water. Add 0.5 mL Probe Rinse. Store solution in glass. Solution should be prepared fresh weekly.

Sample Preparation

1. Frozen samples should be completely thawed the day of analysis.

Preparation for Analysis

1. New reagents should be put into the reagent cups each day. If there is old reagent in the cups, dump them into the appropriate waste container and rinse the reagent cups several times with DI water and then add the refrigerated reagent.
2. The diluent cup should be dumped and replaced with fresh DI water (or extract) each day.
3. The reservoirs on the side of the machine should be full at the start of each day and may need to be refilled if more than one run is done in a day. To refill, rinse the reservoirs several times with DI water. The DI water reservoir needs DI water only. Fill the Probe Rinse reservoir with DI water to the top and then 1 mL of Smartchem Probe Rinse is added. Fill the Cleaning Solution reservoir to 1 L and then add 50 mL Smartchem Cleaning Solution.
4. The Smartchem may need to be turned on & will need to be reset (shut instrument off and restart software) if it is on. The power switch is on the back left side of the instrument. Start up the Smartchem software that is labeled "SmartchemNew". To log in the username is "Westco" and password is "joe".
5. When the software says "Standby" at the bottom of the window, click the "Diagnostic" button on the lower right. Click on the "Miscellaneous" tab and click on "Reset" in the "General" area of the window. After system is finished resetting, click on "Diagnostic" tab again to close. Allow system to go to "Standby" again before proceeding.
6. Wash cuvetts prior to every run and wait 15 minutes for cuvetts to dry before starting the run. This can be done while you are entering samples and preparing the sample racks.
7. If this is the first run with new working standards, then the calculated standard concentrations need to be entered into the Method. Click on "Method" and enter the standards into the appropriate spaces to the right of the window.
8. Click on "Sample Entry" and then start up the appropriate method by double clicking on it at the bottom of the window. In the upper left of the window enter the number of samples and standards that you are going to run and click on the check mark to accept. The method is set up to automatically enter blanks, QC standards, duplicates, and spikes

every 12 samples, so this does not to be included in the amount that you enter. On the right side of the window enter the UNH ID # and standards for your run.

9. In addition to the standards automatically entered, two standards should be run every 12 samples and the full range of working standards should be run at the end of the run. Standards are typically run after the Blanks and QC sample so that duplicates are performed on samples not standards. Names cannot be duplicated, so change names of standards slightly each time you enter them. When finished entering, click the “save” icon at the top right of the window.
10. Name the file as you wish to differentiate between runs. Click “Yes” to print and then click on the printer icon. This will print your run sheet. Attach the run sheet header provided and write in the information that it asks for. Staple the header to the top of the run sheets.
11. Rinse each vial once with sample or standard and then fill between the top two lines of the Smartchem vial.
12. Samples should be placed in the appropriate Smartchem rack and location number, which is indicated on the run sheet. Racks should be placed in the proper position & are keyed to ensure that they are.
13. START the run by clicking on the Play icon in the upper left of the window. Uncheck “RBL” and then check “WBL” to initiate Water Baseline at the beginning of the run. This measures the absorbance of water in the cuvette to account for changes in the cuvette over time and check the condition of the filters and lamp. WBL only needs to be run once a day.
14. After the run has started & the calibration curve window appears, check the “results” page to make sure the calibration curve is acceptable and that the first set of NH₄ and QC standards are recovered appropriately.
15. When run is complete click on “Export” to the left of the window and export to an Excel file.

Quality Assurance and Control

1. Prior to running the Smartchem you must log-in on the Log-In Excel sheet on the Smartchem computer. Please fill-in all designated information. This information will aid in maintenance of the instrument and will be used in conjunction with the Quality Control data.
2. Following completion of your analysis you are responsible for checking the data. The data is to be copied and pasted into the appropriate lab Excel Report Template on the Smartchem computer and the file should be named by date of analysis (described in worksheet). This template will guide you to report the QC results for the run. This includes % recovery of QC standards (CRM), run time check standards, and lab duplicates. Lab % recovery of sample duplicates, run time check standards, and QC standards should be between 85 and 115 % (see WQAL QAPP for more information).
3. When completed copy the Excel file into the lab manager’s directory on the main lab computer. This information, along with the data, will be entered into the WQAL database by the lab manager to create control charts.

Appendix G

NO₃-NO₂ Standard Operating Procedure using SEAL Analytical Discrete Multi-Chemistry Analyzer (AQ2)

Water Quality Analysis Laboratory at the University of New Hampshire

Prepared by: Katie Swan

Date of Last Revision: 4/25/16

Signature of Reviewer/Reviser: _____

Method is based on:

USEPA 353.2 Revision 2.0, August, 1993. Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry.

Protocol NO₃+NO₂

Introduction

The SEAL analytical discrete multi-chemistry auto-analyzer performs the same analytical methods as manual colorimetric assays done on a lab bench. We analyze NO₃+NO₂, PO₄, and TN/TP on surface, ground, soil extracts, and saline waters routinely with this instrument.

The NO₃+NO₂ method is based on USEPA 353.2 Revision 2.0, August, 1993. This method determines the combined nitrate (NO₃) + nitrite (NO₂) present in the sample. Nitrate is reduced to nitrite by passage of a filtered sample through an open tubular copperized cadmium redactor (OTCR). The nitrate reduced to nitrite plus any nitrite originally present in the sample is then determined as nitrite by diazotizing with sulfanilamide followed by coupling with N-(naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye, which is measured colorimetrically at 550 nm.

Preparation of Standards and Reagents

1. Prepare 1000 mg N L⁻¹ NO₃ stock by dissolving 6.0667 g sodium nitrate a 1000 mL volumetric flask and fill to volume. Also, prepare 1000 mg N L⁻¹ NO₂ stock by dissolving 4.926g sodium nitrite in a 1000 mL volumetric flask and fill to volume.
2. If the samples to be analyzed are at the lower end of the concentration range, it may be necessary to make an intermediate standard (100 mg N L⁻¹).
3. Make working standards for by pipetting the appropriate amount of stock (or intermediate standard) into 100 mL volumetric flasks, and bring them to volume. You can put empty 100 mL volumetric flasks directly on the analytical balance, allowing you to know exactly how much stock you are adding. This eliminates the necessity of weighing water (to determine the volume dispensed) before using the adjustable pipettes. Record weighed values in the TN/TP_NO3 Stds electronic file under McDowell Shared in drobox.
4. We typically use 6 working standards ranging 0 to 1.0 mg NO₃-N/L for the NO₃ determination in surface waters. One working NO₂ standard are also needed as a check to ensure that the cadmium coil is reducing NO₃ fully to NO₂. Make the NO₂ standards within the working NO₃ range. This is NO₂ QC in the NO₂ stds working file.
5. Store stock solution in volumetric flask that it was made in and covered securely with Parafilm in the refrigerator. The NO₃ stock will keep for about one (1) month. Working standards can be stored in the volumetric flasks that they were made in. Be sure to cover them tightly with Parafilm. Standards are good for a week or so. Standards should be made weekly, or more frequently if dealing with low concentrations (< 0.3 mg/L).

6. A QC standard reference sample is run along with samples in a run. The QC is made using pre-made SPEX standards that is pipetted for specified amount and weighed out on the analytical balance and diluted to final desired volume. Refer to TN/TP_NO3 electronic file under McDowell Shared file in drobox. Also run a Lamprey CCV, which is a large batch sample from the weekly Lamprey site, as a reference. There should be a bag of them in the freezer as well.
7. Preparation of the working reagents for the method:
 - a. Ammonium Chloride Buffer solution: In a hood, to the dedicated 1L plastic bottle add and dissolve 500 mL DI water, 180 g Ammonium chloride, and 2.0 g disodium EDTA. Adjust the pH to 8.55 with Ammonium hydroxide. Dilute to 1 L and mix.
 - b. Working Buffer solution: To approximately 75 mL of DI water in a 200 volumetric flask add 200 ml of the Ammonium Chloride Buffer solution and 1.0 mL of Triton X-100 solution and dilute to 200 mL with DI water. Transfer the solution to a dark 250 mL plastic bottle. Solution is stable for two weeks.
 - c. Sulfanilamide-NEDD solution: To approximately 250 mL of DI water in a 500 mL volumetric flask dissolve 1.0 g of sodium hydroxide pellets, slowly add 20 mL of phosphoric acid, add 7.5 g of sulfanilamide and 0.375 g of N-(1-naphthyl) ethylene diamine dihydrochloride and stir to dissolve. Dilute to 500 mL with DI water. Solution is stable for six weeks.

Sample Preparation

1. Frozen samples should be completely thawed the day of analysis.

Preparation for Analysis

1. Reagents are poured into the Seal wedges and the reagent name and its position in the wedge tray should be marked. If there are reagents in the wedges and they were kept cold (i.e. in the fridge or in the Seal with it left on in the refrigerated compartment), then they can be reused if it is valid for the reagent to do so. Some reagents might need to be made daily, so please check the method. If they were not refrigerated and left in the wedges, then please dump them into the appropriate waste container and rinse the wedges several times with DI water and replace the reagent.
2. The DI water reagent wedge should be dumped and replaced with fresh DI water (or extract) about once per week.
3. The DI water reservoir on the side of the SEAL should be full at the start of each day and may need to be refilled if more than one run is done in a day. To refill, rinse the reservoir several times with DI water. The DI water reservoir needs DI water only.
4. Change out the appropriate reaction segments (1-10) that need to be changed (i.e. have been used). This can be checked in the "Maintenance" of the Seal software, which will be described below.
5. The SEAL may need to be turned on. The power switch is on the back right side of the instrument. Start up the SEAL software that is labeled "SEAL AQ2". To log in the username is "wrrc lab" and password is "waterlab".

6. When the software opens on the “run screen”, select the “Maintenance and Daily Start Up” tab on the top right of the screen.
 - a. Click on the “Maintenance” tab and the “main maintenance and setup” window will come up. Want to zero reaction segments each run, select “Zero Segments” and select yes. To select desired maintenance function is on the left side of the window.
 - b. Select the “Diluter” tab. The diluter needs to be primed each day to ensure that there are no air bubbles present. To prime the diluter, select the “diluter” tab and select total number of primes (10x) and start prime.
 - c. When finished priming the diluter, then select the “Cuvette functions” tab. The aspiration wash bath needs to be auto washed at the start of the day. Select the total number of washes (2x) and click on the “auto wash” button. Make sure that the aspiration bath is filling up and draining.
 - d. When finished with the auto wash, select the “test aspiration tab”. Take off the cover in the left corner in SEAL and will see an inlet and outlet tubing from the cuvette. The value that is used (e.g. 200) is to ensure that the headspace in the outlet and inlet tubing is about 1 inch from the cuvette. Click on “test aspiration” tab and watch where the headspace is when the test finishes. If need to make adjustments to increase or decrease the headspace in the tubing, increase or decrease the initial value and run the aspiration test again.
 - e. When finished with the test aspiration, select the “extra wash” tab. Make sure to have the cuvette cleaning solution wedge in the first position in the reagent tray on the right side of the seal. Run the extra wash and watch to see if the syringe is pulling up the solution properly (no dripping or beading at the tip). Make sure that the syringe is landing in the right well in the reaction segments.
 - f. When finished with the extra wash, take the cuvette cleaning solution wedge out. Exit the main maintenance and setup screen and select “daily start up.” Hit continue. The daily startup will measure and absorbance and a list eight absorbance readings will be reported on the far right side of the main screen. Record the absorbance values each week and make sure the absorbance values do not drift too much each day. This measures the absorbance of water in the cuvette to account for changes in the cuvette over time and check the condition of the filters and lamp.
7. To prime the cadmium coil (refer to the NO₃+NO₂ method in the SEAL manual).
8. If this is the first run with new working standards, then the calculated standard concentrations need to be entered into the Tests. Click on “Tests” under the maintenance and daily startup tab, select the appropriate method, select calibration, and enter the standards into the appropriate spaces under the manual standards (S1-S7; S1 is a blank).
9. In “Maintenance” make sure that the appropriate tray is selected for the tray that you are going to use.
10. Click on “Scheduling”, select tray number and select reagent set #2, and type in the run file (i.e. 160304NO301). In the upper left of the window select the sample type (standards and unknowns), select standards 1-7 (S1-S7). Then enter the UNH ID # in sample ID, which automatically will be entered as type “unknown”, and enter a rep after every 12 samples and Enter a subset or all of the standards at the end of your run setup without using type “standards”, so that they will be entered as unknowns. The method is set up to automatically enter blanks, QCs, and duplicates every 12 samples, so this does not to be included in the amount that you enter. On the right hand side in the “Requested

Tests” column highlight all the cells that contain samples in that column and then select “NOx” at the top. When finished entering, click the “save” icon at the top left of the window.

11. Select “run” when run is set up and saved. Select the run file for the run and continue.
12. Rinse each vial once with sample or standard and then fill $\frac{3}{4}$ full with the SEAL sample cups (1.2 mL or 2mL sample cups).
13. Samples should be placed in the appropriate SEAL sample tray (57 samples or 100 samples trays). Sample trays should be placed in the proper position and screwed in tightly to ensure the tray is not moving around during the run.
14. START the run by clicking on the “Run” tab and select to continue.
15. After the run has started, check the “calibration” tab to make sure the calibration curve is analyzed and check that it is acceptable after it has run the calibration standards at the beginning. Select the “Data Review” tab and that the first set of NO₂, NO₃ and QC standards are recovered appropriately. If NO₂ recovery is high, may need to re-prime the cadmium coil.
16. When the run is complete, click on “Data Review” to the left of the window, select “Accept All” on the top tabs and export to a document file and save under export file.

Data Export

1. Following completion of your analysis you are responsible for checking the data. The data is to be copied and pasted into the appropriate lab Excel Report Template on the SEAL computer and the file should be named by date of analysis (described in worksheet). This template will guide you to report the QC results for the run. This includes % recovery of QC standards (CRM), run time check standards, and lab duplicates. Lab % recovery of sample duplicates, run time check standards, and QC standards should be between 85 and 115 % (see WQAL QAPP for more information).
2. When completed copy the Excel file into the lab manager’s directory on the main lab computer. This information, along with the data, will be entered into the WQAL database by the lab manager to create control charts.

Shut Down Instrument

1. When finished exporting data, need to shut down the instrument.
 - a. Go to the main screen, click on the seal icon on the upper left corner and choose to exit the software. A window will come up and select both boxes “shutting down instrument overnight? and close program?”
2. Put the reagent tray back in the fridge with the reagents in the wedges.
3. Turn off the lamp on the instrument, leave the reagent cooling tray on.
4. Empty the sample tray (sample in the sink and sample vials in the trash).
5. Empty out the DI water reservoir.

Appendix H

Particulate Nitrogen Standard Operating Procedure using Perkin Elmer 2400

Water Quality Analysis Laboratory at the University of New Hampshire

Prepared by: Jody Potter
Date of Last Revision: 1/30/2019

Signature of Reviewer/Reviser: _____

CHN Analysis Protocol

An accurately measured amount of particulate matter is combusted at 975C using an elemental analyzer. The combustion products are passed over a copper reduction tube. Carbon dioxide, water vapor, and nitrogen are homogeneously mixed at a known volume, temperature and pressure. The mixture is released to a series of thermal conductivity detectors/traps, measuring in turn by difference, hydrogen (as water vapor), C (as CO₂) and N (as N₂).

This assumes you have a homogenous sample that has been ground or sieved. Always have the pan arrests in the raised position when placing or removing items from the weighing tray.

Always close the balance door when not placing or removing items.

Be very careful. Cases of the “shakes” are not allowed.

Calibrating the Micro-Balance

1. Remove all samples and weights from the sample and reference trays.
2. Be sure that the trays are free of debris (there are small brushes in the drawer beneath the balance).
3. Lower the pan arrests.
4. Press the AUTOTARE button and wait until integration (“Int”) is complete.
5. Press the RANGE button until “200 mg” appears on the left display.
6. Raise the pan arrests and place a 100 mg calibration weight on the sample pan (the pan on the right). The calibration weight is in a box labeled “AD6 Kit”, located in the drawer to the left of the balance. DO NOT touch the weight with your fingers. Use the forceps.
7. Lower the pan arrests, and enter 100 on the numeric key pad.
8. Press the CALIB button. Calibration is complete.

Sample Preparation

Filters

Filters for Particulate C and N analysis are prepared by folding them in flat tin disks and compressing them into compact packets using the pellet press. Generally ½ the filter is used for 47 mm filters, and the entire filter is used for 25 mm filters. The weight and volume of water filtered have previously been recorded during the TSS analysis. Please follow the UNH WQAL particulate filtration SOP previous to C and N analysis.

Homogenous ground soil or plant material. These samples must be weighed prior to loading into tin capsules and analyzed.

Using the Micro-Balance

1. Press the RANGE button until it reads 20 mg. This is normally the most appropriate range, although for ultra-low, super-critical weighing, you can use the 2 mg range, though generally not recommended.
2. Place the tare weight on the LEFT tray. This is a small piece of copper wire that weighs approximately as much as a sample tin and tin holder
3. Place a sample tin into a black tin holder (found in the drawer below the micro-balance) and carefully place the combination on the right tray.

4. Lower the pan arrests.
5. Press the AUTOTARE button and wait until integration (“Int” is complete).
6. Raise the pan arrests and remove the tared sample tin and holder.
7. Add 2 mg (+/- 0.5 mg) of you sample to the tin. Be careful not to get any sample material on the outside of the tin. NOTE: For mineral soils, you may add 10 to 20 mg of sample to the tin in order for there to be enough C and N to measure accurately.
8. Place the sample, sample tin and holder on the right weighing tray.
9. Lower the pan arrests and wait for the weight to stabilize.
10. Record weight.
11. Raise pan arrests and remove sample from Micro-Balance.
12. On a clean surface. Fold the top of the tin over to seal it and flatten the bottom of the tin with the butt end of the forceps. Then fold again so it is in thirds.
13. Place the tin so that the area where most of the sample is it facing up. Fold into thirds again so the sample is surrounded by an equal amount of tin. Page 4-61 in the CHN manual shows a modified version of this procedure.
14. Record your sample name and weight on the forms provide and store in a labeled sample tray.

RUNNING THE INSTRUMENT

Gas Flow

Stable and precise gas flow to the CHN analyzer is critical for successful analysis. Prior to starting the CHN analysis, check that all three gas tanks have an **internal pressure of at least 500 psi** (typically the dial on the left). Please inform the lab manager if any of the tanks are below 500 psi, or are close that limit.

Check the regulators (dial on the right) to see that each is set to deliver the appropriate pressure to the instrument.

Helium (He) – The “carrier”, 20 psi.

Air – Runs the pneumatics in the instrument (valves, etc), 60 psi.

Oxygen (O2) – Allows for oxidation of the sample, 16 psi.

Check the Run Counters

1. Press the **PARAMETERS** button.
2. Press **4** and **ENTER**.
 - i. You should see RUN COUNTERS
 REDUCTION ###
 - ii. If this number is less than the number of samples you’re planning to analyze, and is less than 30, you need to fill and install a new reduction tube (see maintenance section). If the number is more than 30, you should run up to that many samples, and plan on changing the reduction tube after that.
3. Press the **ENTER** key.
 - i. You should see RUN COUNTERS

COMBUSTION

- ii. If this number is less than the number of samples you're planning to analyze, and is less than 30, you need to fill and install a new combustion tube (see maintenance section). If the number is more than 30, you should run up to that many samples, and plan on changing the combustion tube after that.
4. Press the **ENTER** key.
 - i. You should see **RUN COUNTERS**
 VRCPT ###
 - ii. If this number is less than the number of samples you're planning to analyze, and is less than 30, you need to replace the vial receptacle (see maintenance section). If the number is more than 30, you should run up to that many samples, and plan on replacing the vial receptacle after that.
5. Press the **ENTER** key again, and you should be back to the **PARAMETERS** prompt.
6. Press **PARAMETERS** button and you should return to **STANDBY**.

System Purge

1. Press the **PURGE GAS** button.
2. You should see **PURGE GAS**
 HELIUM Y/N
3. Press the **YES** button.
4. You should see **PURGE GAS**
 ENTER TIME
5. Enter the time you want to purge in seconds. Typically 180 is sufficient for Helium.
6. Press **ENTER**.
7. You should see **PURGE GAS**
 OXYGEN Y/N
8. Press the **YES** button.
9. You should see **PURGE GAS**
 ENTER TIME
10. Enter the time you want to purge in seconds. Typically 120 is sufficient for Oxygen
11. After the gasses have finished purging, you should be back in **STANDBY**.

Tray Set Up

Your first sample on you tray should be a series of Blanks, Conditioners, and K-factors, in the following order;

1. Blank
2. Blank

9. Enter the appropriate number that describes the sample for the specified position on the sample tray; 1 for Blank, 2 for K-factor, 3 for Sample, or 4 to reset or print.
10. If you enter 1 (blank), you will immediately go to the next sample.
11. If you enter 2 (K-factor), you will see

THEORY STANDARDS
S1 S2 S3 S4

 - i. Enter 1 (S1 = Acetanalide), and then the weight of the standard, and press **ENTER**
12. If you enter 3 (Sample), you will see

ID _
13. You must put some number or letter combination here. It does not need to be unique, or relevant to your sample, but the machine requires a value.
14. The instrument will automatically prompt you for information about the next sample.
15. When you are done entering information for all your samples, press **AUTORUN**, which will put you back at **STANDBY**.
16. With the sample carousel removed from the instrument, turn it so position 60 is over the hole in the bottom of the carousel.
17. Fill your tray with your blanks, standards and samples up to position 59 (leave 60 empty for now).
18. Put the sample carousel on the instrument so that position 60 is lined up with the arrow on the front of the machine, and tighten the knurled nut.
19. Turn the carousel on click clockwise (to the left) so that position 1 is lined up with the arrow.
20. Put sample 60 in position 60.
21. Press the **START** button.

Adding to a Run Sequence

See manual, page 5-117, and is also attached to the protocol in the lab Protocol binder.

Modifying Run Parameters

See manual, page 5-119, and is also attached to the protocol in the lab Protocol binder.

Data Retrieval and Processing

Data from each of your runs is printed out at the completion of each sample. You will need to manually enter this information into an Excel spreadsheet. Your spreadsheet should have at least the following columns and the appropriate information for each sample in your run. Occasionally, the raw signals are useful to correct for a bad blank, or other problem with the run. Don't throw your print out away until you're sure your run is perfect, or you've entered all of the data (including the raw signal values), as there is no other way to retrieve your data once the paper copy is gone.

Tray position	Sample	Weight (mg)	C (mass, blank count,	H (mass, blank count,	N (mass, blank count,
---------------	--------	-------------	-----------------------	-----------------------	-----------------------

			or K-factor)	or K-factor)	or K-factor)

Once you have the mass for C, H, and N, you can easily calculate %C, %N, C:N, mg C or N/L for sediment samples etc. for your sample.

You must also calculate the % recovery of the reference material analyzed in the analysis. The data file should be saved into the lab manager's directory on the main lab computer. This information, along with the data, will be entered into the WQAL database by the lab manager to create control charts.

Appendix I

Ortho-phosphate (PO_4) Standard Operating Procedure SEAL Analytical Discrete Multi-Chemistry Analyzer (AQ2)

Water Quality Analysis Laboratory at the University of New Hampshire

Prepared by: Katie Swan

Date of Last Revision: 4/25/16

Signature of Reviewer/Reviser: _____

Method is based on:

USEPA method 365.3, 1971, modified March 1983. . Determination of Ortho-phosphate by Semi-Automated Colorimetry.

Protocol PO₄

Introduction

The SEAL analytical discrete multi-chemistry auto-analyzer performs the same analytical methods as manual colorimetric assays done on a lab bench. We analyze NO₃+NO₂, PO₄, and TN/TP on surface, ground, soil extracts, and saline waters routinely with this instrument.

The PO₄ method is based on the USEPA method 365.2, 1971, modified March 1983. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorous to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color measured at 880nm is proportional to the phosphorous concentration.

Preparation of Standards and Reagents

1. Prepare 1000 mg N L⁻¹ PO₄ stock by dissolving 4.3937 g potassium phosphate in a 1000 mL volumetric flask and fill to volume.
2. If the samples to be analyzed are at the lower end of the concentration range, it may be necessary to make an intermediate standard (100 mg P L⁻¹).
3. Make working standards for by pipetting the appropriate amount of stock (or intermediate standard) into 100 mL volumetric flasks, and bring them to volume. You can put empty 100 mL volumetric flasks directly on the analytical balance, allowing you to know exactly how much stock you are adding. This eliminates the necessity of weighing water (to determine the volume dispensed) before using the adjustable pipettes. Write down how much standard was added & give to lab manager. We typically use 6 working standards ranging 0 to 200 µg PO₄-P/L for the PO₄ determination in surface waters.
4. Store stock solution in clean, airtight, glass container in the refrigerator. The PO₄ stock will keep for about one month. Working standards can be stored in the volumetric flasks that they were made in. Be sure to cover them tightly with Parafilm. Standards are good for a week or so. Standards should be made weekly, or more frequently if dealing with low concentrations (< 200 µg/L).
5. A QC standard reference sample is run along with samples in a run. The QC is made using pre-made SPEX standards that is pipetted for specified amount and weighed out on the analytical balance and diluted to final desired volume. Refer to PO₄ electronic file under McDowell Shared file in drobox. Also run a Lamprey QC, which is a large batch sample from the weekly Lamprey site, as a reference. There should be a bag of them in the freezer as well.
6. Preparation of the working reagents for the method:
 - a. Sulfuric acid solution, 5N: Slowly add 70 mL of concentrated H₂SO₄ to 400 mL DI water. Cool to room temperature and dilute to 500 mL.

- b. Antimony potassium tartrate solution (0.3%): Weigh 0.30 g Antimony potassium tartrate in 75 mL of DI water, dilute to 100 mL in dedicated plastic bottle. Prepare fresh monthly.
- c. Ammonium molybdate solution (4%): Dissolve 4 g Ammonium molybdate tetrahydrate in 75 mL DI water, dilute to 100 mL in dedicated plastic bottle. Discard reagent if becomes turbid or discolored.
- d. Working Ascorbic Acid: Dissolve 1.5 g Ascorbic acid in 80 mL of DI water. Add 2 mL of 15% SDS solution, dilute to 100 mL of DI water. Prepare this solution fresh daily.
- e. Color Reagent: To a clean 125 mL plastic bottle add 75 mL of prepared 5N sulfuric acid and then add 18.0 mL Ammonium molybdate solution and mix. Add 7.5 mL Antimony potassium tartrate solution and mix. Add 4 mL 15% SDS and dilute to 100 mL with DI water. Mix. This solution should be prepared every 3 weeks.

Sample Preparation

1. Frozen samples should be completely thawed the day of analysis.

Preparation for Analysis

1. Reagents are poured into the Seal wedges and the reagent name and its position in the wedge tray should be marked. If there are reagents in the wedges and they were kept cold (i.e. in the fridge or in the Seal with it left on in the refrigerated compartment), then they can be reused if it is valid for the reagent to do so. Some reagents might need to be made daily, so please check the method. If they were not refrigerated and left in the wedges, then please dump them into the appropriate waste container and rinse the wedges several times with DI water and replace the reagent.
2. The DI water reagent wedge should be dumped and replaced with fresh DI water (or extract) each day.
3. The DI water reservoir on the side of the SEAL should be full at the start of each day and may need to be refilled if more than one run is done in a day. To refill, rinse the reservoir several times with DI water. The DI water reservoir needs DI water only.
4. Change out the appropriate reaction segments (1-10) that need to be changed (i.e. have been used). This can be checked in the "Maintenance" of the Seal software, which will be described below.
5. The SEAL may need to be turned on. The power switch is on the back right side of the instrument. Start up the SEAL software that is labeled "SEAL AQ2". To log in the username is "wrrc lab" and password is "waterlab".
6. When the software opens on the "run screen", select the "Maintenance and Daily Start Up" tab on the top right of the screen.
 - a. Click on the "Maintenance" tab and the "main maintenance and setup" window will come up. Want to zero reaction segments each run, select "Zero Segments" and select yes. To select desired maintenance function is on the left side of the window.

- b. Select the “Diluter” tab. The diluter needs to be primed each day to ensure that there are no air bubbles present. To prime the diluter, select the “diluter” tab and select total number of primes (10x) and start prime.
 - c. When finished priming the diluter, then select the “Cuvette functions” tab. The aspiration wash bath needs to be auto washed at the start of the day. Select the total number of washes (2x) and click on the “auto wash” button. Make sure that the aspiration bath is filling up and draining.
 - d. When finished with the auto wash, select the “test aspiration tab”. Take off the cover in the left corner in SEAL and will see an inlet and outlet tubing from the cuvette. The value that is used (e.g. 200) is to ensure that the headspace in the outlet and inlet tubing is about 1 inch from the cuvette. Click on “test aspiration” tab and watch where the headspace is when the test finishes. If need to make adjustments to increase or decrease the headspace in the tubing, increase or decrease the initial value and run the aspiration test again.
 - e. When finished with the test aspiration, select the “extra wash” tab. Make sure to have the cuvette cleaning solution wedge in the first position in the reagent tray on the right side of the seal. Run the extra wash and watch to see if the syringe is pulling up the solution properly (no dripping or beading at the tip). Make sure that the syringe is landing in the right well in the reaction segments.
 - f. When finished with the extra wash, take the cuvette cleaning solution wedge out. Exit the main maintenance and setup screen and select “daily start up.” Hit continue. The daily startup will measure and absorbance and a list eight absorbance readings will be reported on the far right side of the main screen. Record the absorbance values each week and make sure the absorbance values do not drift too much each day. This measures the absorbance of water in the cuvette to account for changes in the cuvette over time and check the condition of the filters and lamp.
7. If this is the first run with new working standards, then the calculated standard concentrations need to be entered into the Tests. Click on “Tests” under the maintenance and daily startup tab, select the appropriate method, select calibration, and enter the standards into the appropriate spaces under the manual standards (S1-S7; S1 is a blank).
 8. In “Maintenance” make sure that the appropriate tray is selected for the tray that you are going to use.
 9. Click on “Scheduling”, select tray number and select reagent set #1, and type in the run file (i.e. 160304NO301). In the upper left of the window select the sample type (standards and unknowns), select standards 1-7 (S1-S7). Then enter the UNH ID # in sample ID, which automatically will be entered as type “unknown”, and enter a rep after every 12 samples and Enter a subset or all of the standards at the end of your run setup without using type “standards”, so that they will be entered as unknowns. The method is set up to automatically enter blanks, QCs, and duplicates every 12 samples, so this does not to be included in the amount that you enter. On the right hand side in the “Requested Tests” column highlight all the cells that contain samples in that column and then select “op1” at the top. When finished entering, click the “save” icon at the top left of the window.
 10. Double click “run” when run is set up and saved. Select the run file for the run and continue.

11. Rinse each vial once with sample or standard and then fill $\frac{3}{4}$ full with the SEAL sample cups (1.2 mL or 2mL sample cups).
12. Samples should be placed in the appropriate SEAL sample tray (57 samples or 100 samples trays). Sample trays should be placed in the proper position and screwed in tightly to ensure the tray is not moving around during the run.
13. START the run by clicking on the “Run” tab and select to continue.
14. After the run has started, check the “calibration” tab to make sure the calibration curve is analyzed and check that it is acceptable after it has run the calibration standards at the beginning. Select the “Data Review” tab and that the first set of QC standards are recovered appropriately.
15. When the run is complete, click on “Data Review” to the left of the window, select “Accept All” on the top tabs and export to a document file and save under export file.

Data Export

1. Following completion of your analysis you are responsible for checking the data. The data is to be copied and pasted into the appropriate lab Excel Report Template on the SEAL computer and the file should be named by date of analysis (described in worksheet). This template will guide you to report the QC results for the run. This includes % recovery of QC standards (CRM), run time check standards, and lab duplicates. Lab % recovery of sample duplicates, run time check standards, and QC standards should be between 85 and 115 % (see WQAL QAPP for more information).
2. When completed copy the Excel file into the lab manager’s directory on the main lab computer. This information, along with the data, will be entered into the WQAL database by the lab manager to create control charts.

Shut Down Instrument

1. When finished exporting data, need to shut down the instrument.
 - a. Go to the main screen, click on the seal icon on the upper left corner and choose to exit the software. A window will come up and select both boxes “shutting down instrument overnight? and close program?”
2. Put the reagent tray back in the fridge with the reagents in the wedges.
3. Turn off the lamp on the instrument, leave the reagent cooling tray on.
4. Empty the sample tray (sample in the sink and sample vials in the trash).
5. Empty out the DI water reservoir.

