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

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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 (SiO_2) 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 (+/- 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 = abs(dup1-dup2)/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 SiO2/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.