

Quality Assurance Project Plan

Sample Analysis for the Northeast Temperate Network and Acadia National Park

Dr. Jasmine Saros and Michael Handley, University of Maine

Sawyer Water Research Laboratory (SWRL)
Climate Change Institute
University of Maine
5764 Sawyer Environmental Research Center
Orono, ME 04469

List of Tables

- Table 1. Target Holding Times, Method Detection Limits and Precision and Accuracy Objectives
- Table 2. Sample Processing and Preservation
- Table 3. Analytical Methods for the Sawyer Water Research Laboratory
- Table 4. Equations for Routine Calculations

Introduction

Project Description

The activities by the University of Maine will be in support of the Northeast Temperate Network Project and Acadia National Park Long Term Monitoring Projects. The scope may change, depending on needs of The National Park Service. This QA plan details the operations of the Sawyer Water Research Laboratory of the University of Maine. Project analytes will be: closed cell pH, equilibrated pH (standard CO₂ air), ANC, specific conductance, DOC, true color and apparent color, Ca, Mg, K, Na, Al, NH₄, Cl, NO₂⁻, NO₃, SO₄, total P, total N, and chlorophyll *a* (Chl *a*). Calculated variables will include ion and conductance balances. Other empirical relationships will be examined at the University of Maine to verify analytical results, or to identify questionable results for sample re-analysis.

Objectives for Measurement

Data Quality Objectives (DQO) are listed in Table 1 and are defined below.

Definition of Precision

Precision is a measure of mutual agreement, characteristic of independent measurements resulting from repeated application of the process under specified conditions (Taylor, 1987). The coefficient of variation (CV), also known as the percent relative standard deviation (RSD), is used to estimate precision.

$$CV = (s/\bar{x}) * (100)$$

S= sample standard deviation

$\bar{x}$ = arithmetic mean

Precision can be partitioned in several ways:

Analytical precision refers to precision of the analysis performed by analytical laboratory instruments; it is estimated by laboratory replicates. Analytical precision can be estimated for within-batch precision if laboratory replicates are measured within the same analytical batch, or for among-batch precision if laboratory replicates are measured in different batches. A batch is a set of samples analyzed with the same calibration curve.

Definition of Accuracy and Bias

Accuracy is the degree of agreement of a measured value with the true or expected value of the quantity of concern (Taylor, 1987). Accuracy is expressed as the percent difference from the reference value $(100 (X-T) / T)$, where X is the measured value and T is the reference value. Accuracy is estimated for the analytical system, for both within- and among-batch.

Bias is a systematic error inherent in a method or caused by some artifact of the measurement system (Taylor, 1987). Participation in performance audits by SWRL is outlined below.

Sampling Procedures

Glass and Plasticware Preparation

All plasticware and aliquot bottles are high density polyethylene (HDPE). Acid-washing entails (1) soaking or rinsing articles in 10% solution of hydrochloric acid, (2) rinsing with deionized water, (3) soaking with deionized water and rinsing at least 3 times with deionized water. Bottles are dried under a HEPA filter, capped, and stored. Glass containers are allowed to drain dry and are then sealed.

Sample Collection

Sample collection is the responsibility of field crews and is not discussed here.

Field Filtered Samples: Samples for Chlorophyll *a* are field filtered through 0.45 μm Millipore Nitrocellulose Membrane Filters in replicate.

Unfiltered samples: Samples for pH, ANC, Total P, Total, N, apparent color are not filtered.

Filtered samples: Aliquots for anions, cations, Al, NH_4 , NO_2^- , DOC, and true color are filtered through 0.4 μm membrane filters.

Samples are filtered using vacuum filtration with a plastic magnetic filter apparatus and collection flask. Filters are rinsed first with at least 50 ml deionized water, then at least 10 ml of sample. These rinses also serve to rinse the collection flask. A new filter is used for each sample; several filters are sometimes necessary to obtain sufficient volume for analyses for especially high DOC samples.

Chlorophyll *a* sample filters are folded, wrapped in aluminum foil, labeled with sample name date and volume filtered, then stored in a freezer for up to 28 days.

The cation and Al aliquots are acidified with nitric acid to give a sample acid concentration of 1% (v/v). All samples and aliquots are refrigerated until processing or analysis. A summary of preservation methods is provided in Table 2.

Sample Custody

Sample Identification Codes

All samples will be uniquely labeled by field staff. These codes will be transferred to aliquot bottles in the Sawyer Environmental Research Laboratory.

Laboratory Data Evaluation

Charge balances, ion ratios, and other chemical relationships which aid in identifying outliers are calculated. These results are examined to decide whether samples should be rerun if volume permits.

Calibration Procedures and Frequency

Calibration standards are prepared from American Chemical Society (ACS) reagent grade chemicals or commercially available stocks of a certifiable grade. All water used in the preparation of standards meets the specifications of ASTM Type 1.

Major Instrumentation (Ion Chromatograph, ICP-MS, Carbon Analyzer, and Autoanalyzer)

Initial Calibrations: An appropriate number of calibration points is used for each instrument, based on the requirements of the instrument. If the sample concentration is above the range of calibration standards used, analyses are repeated using either a higher concentration standard or by diluting the samples. If sample concentrations fall below the range of calibration standards and above the specified detection limit, then a lower concentration calibration standard is used. Instruments are calibrated prior to each run.

Recalibrations: An unacceptable value for reference material or calibration standard requires the recalibration of the instrument along with the re-analysis of all samples subsequent to the last acceptable reference material or calibration standard value. If further unacceptable values are produced, analyses will cease until the problem is corrected.

pH Electrodes

Electrodes for pH measurement are stored in the solution recommended by the manufacturer. The electrode is calibrated using a 2 point (pH 4 and pH 7) calibration technique. If an electrode response slope less than 98% is obtained, that electrode is not used. Electrode performance in low ionic strength water is verified daily by analysis of standardized acid or buffer.

Automatic ANC Titrator

ANC titrations use acid that has been standardized against a standard base, which in turn has been standardized against a primary standard of potassium hydrogen phthalate. A blank and standard are run in each batch of 18 samples.

Conductivity Meter

The conductivity meter is checked before each run, measuring the conductivity of several conductivity standards.

Color

Color is determined spectrophotometrically, at a wavelength of 457.5 nm in a 10 cm cell. A calibration curve for the spectrophotometer is drawn by plotting the absorbance of a range of PtCo color standards.

Chlorophyll a

Chlorophyll *a* is determined spectrophotometrically, at wavelengths 630, 647, 664, and 750 nm in a 10-cm cell. The spectrophotometer is zeroed using a blank, a method blank, and a method spike. These ensure instrument is zeroed correctly.

Analytical Procedures

Analytical procedures are listed in Table 3.

Data Reduction, Validation, and Reporting

Data Reduction/ Screening

After all analyses for a given period have been completed, charge balances and the conductance balance are calculated. If problems are found, samples are rerun if sample volume permits. If problems remain after reanalysis, a note is made with the sample.

Internal Quality Control Procedures

Several types of samples are introduced during sample preparation and analysis to assess precision and accuracy at specific stages in the analytical process.

An analytical batch is the group of samples analyzed with the same instrument calibration. Each analytical batch has the following QC samples:

- A QC sample at a concentration that is between 25% and 75% of the calibration range and prepared from a source independent from the calibration standards.
- A laboratory blank sample; reagent blank samples are required for measurements of total P and total N.
- An analytical replicate which is prepared at the instrument.
- Matrix spikes are done for new or problematic matrices.

QC Sample

To check for accuracy during analysis, reference samples containing appropriate analytes at concentrations simulating natural surface waters are prepared for analyzed species. External sources of reference samples are used when available. The QC samples are used by the analyst to

ensure the analytical process is in control. These samples are analyzed immediately after calibration, after every 10 to 15 samples, and at the end of the analytical batch. Each measurement is expected to be within accuracy objectives. Accuracy calculations are given in Table 4. Additionally, QC samples are recorded on a control chart.

Laboratory Blank Sample

Laboratory blank samples are made for each analyte requiring sample preparation. These samples indicate control of contamination during sample preparation. The laboratory blank is made from reagent grade water and is prepared in the same manner as a sample. A single laboratory blank is generated for each sample preparation batch. For samples not requiring preparation, a laboratory blank is generated for each sample preparation batch. For samples not requiring preparation, a laboratory blank is used to monitor background changes in measurement systems; e.g. turbidity and total suspended solids. Reagent blanks are prepared for total P and total N. These are made from reagent grade water and treated in an identical fashion to samples prepared for these tests. Laboratory and reagent blanks are expected to measure less than twice the analytical detection limit.

Analytical Replicates

Analytical replicates are samples that have been collected, filtered, and preserved as one sample, but analyzed on an analytical instrument at separate times. Analytical replicates are used to estimate analytical precision and are analyzed at a frequency equal to 5 percent of the total sample number. Analytical replicates are expected to meet precision objectives. Precision calculations are given in Table 4.

Matrix Spike Samples

Matrix spike samples are anticipated for total N and total P. A matrix spike is prepared by spiking a split sample with a known amount of analyte. The spike concentration is approximately equal to the expected endogenous level of the analyte. The volume of spike added is negligible. The matrix spike recovery objective is $100\% \pm 15\%$. The formula for matrix spike recovery is given in Table 4.

Analytical Detection Limit

Measurement of the analytical detection limit on a regular basis is necessary for monitoring programs in order to provide regular assessment of instrument performance, as well as quantifiable concentration that will indicate when a measured value is above zero and is in fact detectable by the analytical instrument. The analytical detection limit is defined as one-sided 99 percent confidence interval from repeated measurements of a low-level standard across several calibration curves. The concentration of the low-level check standard should be three to five times the required detection limit (see Table 1). The low-level check standard will be used to monitor batch-to-batch detection limits. The actual instrument detection limit should be measured semiannually. This concentration is the actual instrument detection limit.

Laboratory Practices

Good laboratory practices follow, including:

- Analytical balances are serviced at regular intervals. National Institute of Standards and Technology (NIST) certified weights (class “S” or better) are used to check the accuracy of a balance prior to each use for preparing standards.
- Deionized water system quality is continually monitored for resistivity of 18.2 Mohms and documented.
- Fume hood efficiency is monitored annually and verified routinely.
- Refrigerator temperatures are monitored.
- All containers used in the laboratory are labeled. Chemicals are dated when received and expiration dates checked. All solutions prepared are labeled with contents, date prepared, and initials of technician.

Performance and System Audits

Performance Evaluation Samples

Performance evaluation (audit) samples are used to estimate intralaboratory analytical precision and accuracy, and to estimate interlaboratory precision and bias.

Long Range Transport of Airborne Pollutants Interlaboratory Comparison Studies

The Sawyer Water Research Laboratory participates in the Canada Centre for Inland Waters Long Range Transport of Airborne Pollutants (LRTAP) Interlaboratory Comparability Studies. The purpose of the LRTAP comparability studies is to monitor laboratory performance over time. Three studies are conducted each year with approximately 100 participating laboratories. Ten low ionic strength natural water samples are included in each study.

A median value for each variable for each sample is determined. Descriptive flags are assigned to variables whose values are outside the acceptable limits for difference from the median value. The acceptable limits for each flag class for each variable are based on results from earlier LRTAP studies.

Laboratory rankings of the results from the 10 samples in each study are used to identify bias for each variable for each laboratory. Bias classes are assigned to a variable based on the procedure described by Youden (1969). A summary sheet is prepared by the LRTAP staff after each study for each laboratory and submitted to the participants and Sawyer Water Research Laboratory,

indicating the results (flags and bias) for each variable. Participants are contacted to discuss results and identify necessary corrective actions.

Specific Routine Procedures Used to Assess Data Precision, Accuracy and Completeness

Routine calculations performed as part of QA and data validation are listed in Table 4. These calculations are the same as those used by Hillman et al. (1986), and are specified in the Watershed Manipulation Project: Integrated Quality Assurance Plan: FY87-89 (Ericksen et al, 1990).

Corrective Action

QC Samples

QC samples are expected to meet accuracy objectives; when they do not, analysis will halt until the situation is corrected and control is verified by analysis of QC samples which meet accuracy objectives.

Laboratory Blank Samples

In all cases, the concentration of measured analyte in blank samples should be less than twice the detection limit for the analyte under investigation. “High” blanks (more than twice the detection limit) are regarded as evidence of contamination and all relevant samples are reprocessed when possible, or flagged in the dataset if re-analysis is not feasible.

Laboratory Replicates

Relative standard deviations for laboratory splits and replicates will be calculated and should fall within the objectives presented in Table 1. Replicate violations require investigation and reanalysis. Split violations require re-preparation.

Matrix Spike Sample

Matrix spike percent recovery from the laboratory matrix spike samples is evaluated by calculating percent difference. Recovery is expected to be within the QA objective for accuracy for the analyte.

References

American Society of Testing and Materials. 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D1193-77 (Reapproved 1983). ASTM, Philadelphia, PA.

Driscoll, C.T., and J.J. Bisogni. 1983. Weak acid/base systems in dilute acidified lakes and streams of the Adirondack region of New York State. Modeling Total Acid Precipitation Impact. In: J.L. Schooner (ed.), Ann Arbor Science Publishers, pp. 53-72.

Erickson, H.E., M.M. Morrison, J.S. Kern, L.E. Hughes, J.T. Malcolm and K.W. Thronton. 1990. Watershed Manipulation Project: Integrated Quality Assurance Plan: FY87-89. Draft, U.S. Environmental Protection Agency, Corvallis, OR.

Hillman, D.C., J.F. Potter and S.J. Simon. 1986. National Surface Water Survey, Eastern Lakes Survey Phase I – Analytical Methods Manual. EPA 600/ 4-86/ 009. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Las Vegas, NV.

Tabatabai, M.A., and W.A. Dick. 1983. Simultaneous determination of nitrate, chloride, sulfate, and phosphate in natural waters by ion chromatography. Journal of Environmental Quality. 12:209-213.

Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Chelsea, MI.

Youden, W.J. 1969. Ranking Laboratories by Round-Robin Tests, In Precision Measurement and Calibration, H.H. Ku, (ed). NBS Special Publication 300, Vol. 1. U.S. Government Printing Office, Washington, D.C.

Table 1. Target holding times, method detection limits, and precision and accuracy objectives

Analyte	Holding Time ¹	Detection Limit ²	Concentration Range	Precision Objective ³	Accuracy Objective ⁴
pH, closed system	48 hours	N/A	<5.74 SU >5.75 SU	± 0.075 SU ± 0.15 SU	± 0.025 SU ± 0.05 SU
pH, equilibrated	14 days	N/A	-Same as for closed systems pH-		
ANC	14 days	N/A	<100 µeq/L >100 µeq/L	± 5 µeq/L ± 5%	± 4 µeq/L ± 4%
Conductivity	14 days	N/A	<50 µS/cm >50 µS/cm	± 1 µS/cm ± 2%	± 1.0 µS/cm ± 2%
DOC	14 days	0.1 mg/L	<2 mg/L >2 mg/L	± 0.1 mg/L ± 5%	± 0.1 mg/L ± 5%
Al	28 days	10 µg/L	<100 µg/L >100 µg/L	± 10 µg/L ± 10%	± 5 µg/L ± 5%
NO ₂ ⁻	48 hours	1.0 µg/L	<20 µeq/L >20 µeq/L	± 1.0 µg/L ± 5%	± 1.0 µg/L ± 5%
Ca	28 days	1.0 µeq/L	<20 µeq/L >20 µeq/L	± 1.0 µeq/L ± 5%	± 0.8 µeq/L ± 4%
Mg	28 days	0.8 µeq/L	<16 µeq/L >16 µeq/L	± 0.8 µeq/L ± 5%	± 0.6 µeq/L ± 4%
Na	28 days	0.9 µeq/L	<20 µeq/L >20 µeq/L	± 1.0 µeq/L ± 5%	± 0.8 µeq/L ± 4%
K	28 days	1.0 µeq/L	<20 µeq/L >20 µeq/L	± 1.0 µeq/L ± 5%	± 0.8 µeq/L ± 4%
NH ₄	28 days	1.1 µeq/L	<20 µeq/L >20 µeq/L	± 1.0 µeq/L ± 5%	± 0.8 µeq/L ± 4%
Cl ⁻	28 days	0.8 µeq/L	<20 µeq/L >20 µeq/L	± 1.0 µeq/L ± 5%	± 0.8 µeq/L ± 4%
NO ₃ ⁻	7 days	0.5 µeq/L	<10 µeq/L >10 µeq/L	± 0.5 µeq/L ± 5%	± 0.4 µeq/L ± 4%
SO ₄ ²⁻	28 days	1.0 µeq/L	<20 µeq/L >20 µeq/L	± 1.0 µeq/L ± 5%	± 0.8 µeq/L ± 4%
Total P	28 days	1 µg/L	<20 µg/L >20 µg/L	± 1 µg/L ± 5%	± 0.8 µg/L ± 4%
Total N ⁵	28 days	1 µg/L	<20 µg/L >20 µg/L	± 1 µg/L ± 5%	± 0.8 µg/L ± 4%
True Color	48 hours	N/A	<50 PCU >50 PCU	± 5 PCU ± 10%	± 5 PCU ± 5%
Apparent Color	48 hours	N/A	<50 PCU >50 PCU	± 10 PCU ± 20%	± 10 PCU ± 5%
Chlorophyll <i>a</i>	28 days	N/A	<10 µg/L >10 µg/L	± 1 µg/L ± 10%	± 1 µg/L ± 10%

¹Holding time is the time from sample collection to analysis; the laboratory will receive most samples 24 to 48 hours after sample collection.

²The method detection limit is determined as one-sided 99 percent confidence interval from repeated measurements of a low-level standard across several calibration curves.

³Precision is estimates as the standard deviation of repeated measurement at lower concentrations, and as percent relative standard deviation at higher concentrations.

⁴Accuracy is estimated as the difference between the measured and target values of performance evaluation samples at lower concentrations, and as the percent difference at higher concentrations.

⁵Methods development is expected for these analytes.

Table 2. Sample Processing and Preservation

Variable	Sample Preservation
True color	Filter through 0.4 μm polycarbonate; Store at 4°C
pH, closed	Store in syringe at 4°C
pH, equilibrated	Aliquot into 500 ml HDPE; Store at 4°C
ANC	Aliquot into 500 ml HDPE; Store at 4°C
Specific conductance	Aliquot into 500 ml HDPE; Store at 4°C
DOC	Filter through 0.4 μm polycarbonate; Store at 4°C
Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , Al	Filter through 0.4 μm polycarbonate; Acidify with HNO_3 to $\text{pH} < 2$; Store at room temperature
NH_4^{+}	Filter through 0.4 μm polycarbonate; Store at 4°C
SO_4^{2-} , Cl^{-} , NO_3^{-} , NO_2^{-}	Filter through 0.4 μm polycarbonate; Store at 4°C
Total P	Aliquot upon arrival into glass
Total N	Aliquot upon arrival into glass
Apparent color	Store at 4°C
Chlorophyll <i>a</i>	Filter through 0.45 μm membrane filters. Wrap in aluminum foil and store in -21°C freezer

Table 3. Analytical Methods for the Sawyer Water Research Laboratory

Variable	Analytical Method Information
ANC	Gran Titration Section 5 ¹
SO ₄	IC, Ion chromatography Section 11 ¹
NO ₃	IC, Ion chromatography Section 11 ¹
Cl	IC, Ion chromatography Section 11 ¹
Ca	ICP-MS Method 3125 B ²
Mg	ICP-MS Method 3125 B ²
Na	ICP-MS Method 3125 B ²
K	ICP-MS Method 3125 B ²
Al	ICP-MS Method 3125B ²
NO ₂ ⁻	4500-NO ₂ -B Colorimetric ²
DOC	5310B High temperature combustion ²
NH ₄	Flow Injection Section 10 ¹
pH, closed	Electrode Section 19 ¹
pH, aerated	Electrode
Specific Conductance	Wheatstone Bridge Section 23 ¹
True Color	Spectrophotometer, 457.5 nm, filtered sample
Chlorophyll <i>a</i>	Spectrophotometric Determination ²
Total P	Persulfate digest Method 4500-P-E ²
Total N	Persulfate digest, cadmium reduction Section 18 ¹

¹Handbook of Methods for Acid Deposition Studies Laboratory Analyses for Surface Water Chemistry EPA 600/4-87/026 September 1987

²Standard Methods for the Examination of Water and Wastewater 20th Edition

Table 4. Equations for Routine Calculations

$$1. \text{ Accuracy} = \frac{\text{Determined Value} - \text{Reference Value}}{\text{Reference Value}} * 100$$

$$2. \text{ Precision} = \frac{\text{Standard Deviation}}{\text{Mean}} * 100$$

$$3. \text{ Ion Percent Difference} = \text{IPD} = \frac{\text{Anion} - \text{Cation}}{\text{Anion} + \text{Cation}} * 100$$

$$4. \text{ Conductance Percent Difference} = \text{CPD} \\ = \frac{(\text{Calculated Conductance} - \text{Measured Conductance})}{\text{Measured Conductance}} * 100$$

When measured conductance $\leq 10 \mu\text{S/cm}$, reanalyze if $\text{CPD} > \pm 65\%$;

When $10 \mu\text{S/cm} < \text{measured conductance} \leq 30 \mu\text{S/cm}$, reanalyze if $\text{CPD} > \pm 45\%$;

When $30 \mu\text{S/cm} < \text{measured conductance} \leq 50 \mu\text{S/cm}$, reanalyze if $\text{CPD} > \pm 35\%$; and

When measured conductance $> 50 \mu\text{S/cm}$, reanalyze if $\text{CPD} > \pm 20\%$.

$$5. \% \text{ Spike Recovery} = \frac{(\text{Value of sample} + \text{spike}) - \text{Value of unspiked sample}}{\text{Value of spike added}} * 100$$
