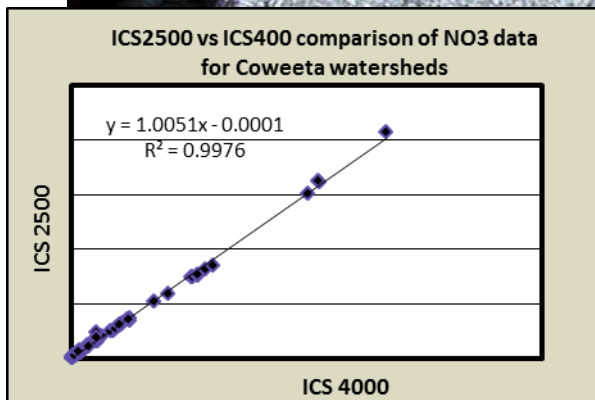
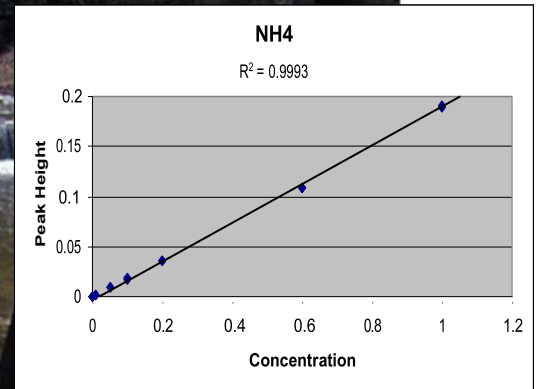
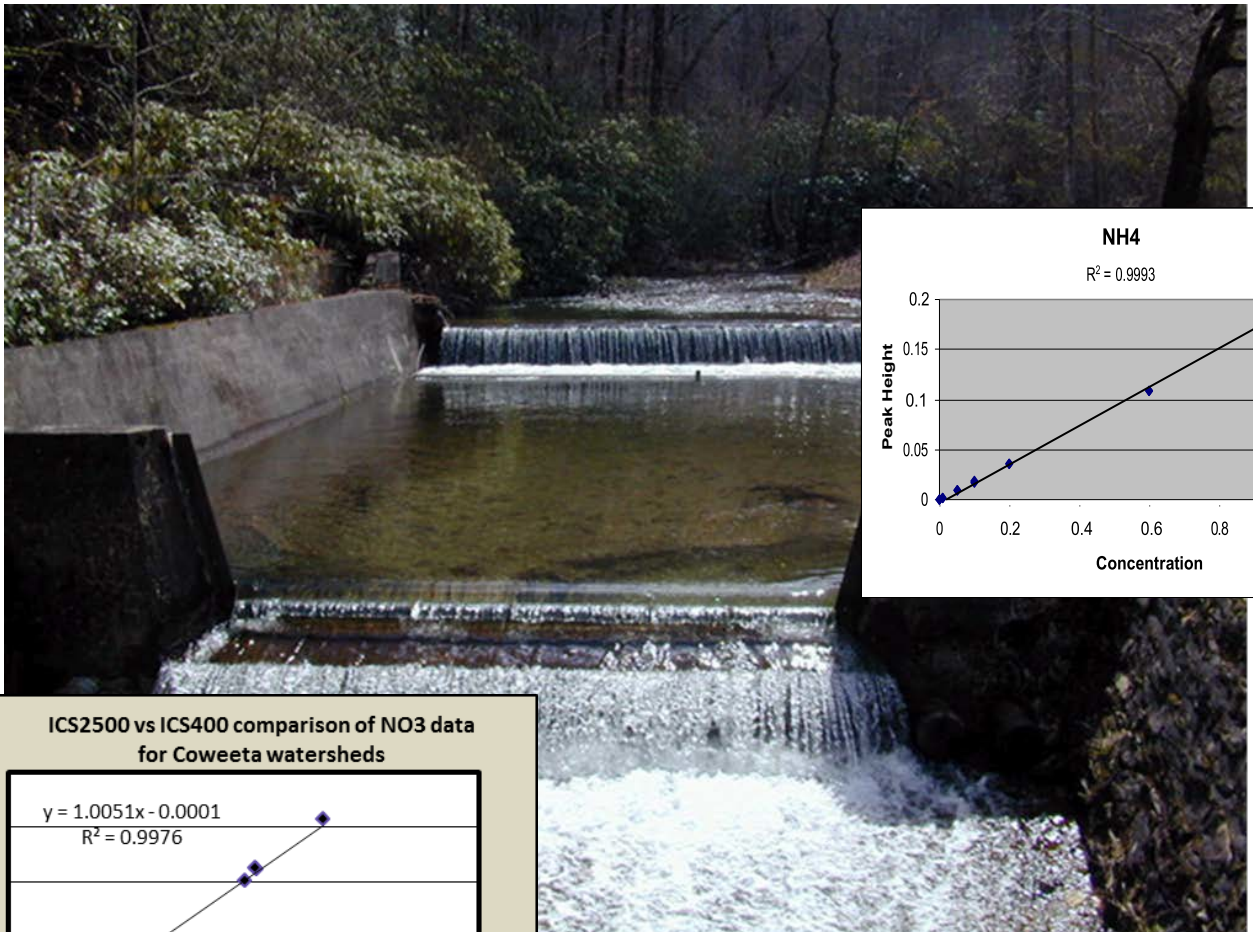


Coweeta Hydrologic Laboratory

QUALITY ASSURANCE PROTOCOL

Revised April 06, 2021



Quality Assurance = A strategy of prevention Quality Control = A strategy of detection

The management of Coweeta Hydrologic Laboratory (CHL) is fully committed to the maintenance of an effective quality assurance program to preserve the integrity of all data collected and reported at CHL. Within the quality assurance program are quality control procedures for each analysis.

Cindi Brown

Laboratory Manager, Laboratory Quality Assurance Officer

Charles A. Doloff

Project Leader

04/06/21

Date

All analyses performed at Coweeta Hydrologic Laboratory (CHL) must follow quality assurance guidelines. The following are sample types analyzed at CHL.

Water:

Watershed
Rain gauge
Lysimeter
Stream grab
Stream
Sigma stream samples
Overland flow
Wells

Soils

Plant Tissue:

Roots
Leaves
Wood
Tree increment cores
Litterbag
Forest Floor

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Quality Assurance Requirements

I. Field Measurements, Sample Collection, Sampling Frequency and Chain of Custody

A. Field Measurements and Sample Collection

1. A field measurement or collected sample must be representative of the parameter or material that is to be analyzed.
2. The primary investigator assigns the sample identity (ID).
3. Field sampling should include procedures to prevent cross contamination.
4. A blank is included with all collection of samples. For example: Watershed collection includes a DI filled bottle carried by the technician during collection.
5. Replicate samples are collected for heterogeneous material such as soil and forest floor as dictated by the study plan.
6. Before placed out in the field, lysimeters are cleaned with 10% HCl and rinsed with deionized water (DI) until the conductivity is below $5\mu\text{mho cm}^{-1}$. The lysimeter is shown to be stable before data are recorded by repeated sampling and analysis.

B. Sampling frequency is dictated by the research objectives as defined in the study plan.

C. A Request for Analytical Services (see [Appendix A](#)) must be completed by the investigating scientist, authorized by the project leader, and presented to the lab manager before samples can be analyzed.

D. Chain of Custody

1. Scientist submits samples to the lab.
2. The project leader assigns sample priority.
3. The lab manager assures sample flow and disposition.

II. Preparation, Labeling, and Storage of Samples

A. Some samples require the addition of a preservative to increase the shelf life of the sample.

See [Appendix B](#) for a list of sample matrix type and shelf life. See Appendix C for a list of preservation techniques and maximum shelf life for several parameters.

B. Field technicians assure proper labeling of the sample, which include sample ID, date of collection, and the name of the principal investigator.

C. Stream, lysimeter and collected water samples are stored in the Walk in Cooler. The cooler is kept at a temperature of $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Perishable samples, defined as samples not treated with a preservative, are run within the specified shelf life (see [Appendix B](#)). If the sample cannot be analyzed within the specified shelf life the sample is frozen at -18°C . Frozen samples must include 3 DI blanks.

D. Extracted NH_4Cl , KCl , NH_4Ac and double acid samples, can be unstable. Therefore, the shelf life is determined and documented (see [Appendix B](#)). The samples are run before the shelf life is exceeded.

E. The specific shelf life will be determined for all new sample matrices. See [Appendix B](#).

F. Freshly collected Soil samples are stored in the Walk in Cooler until ready for process.

G. Soil samples to be dried are stored in the insulated attic above the lab.

H. Extracted soil samples are stored in the refrigerator nearest to the lab in which analysis will be performed (i.e. extracted samples for cation analysis are stored in the refrigerator located in the ICP lab).

- I. Plant tissue samples are stored in airtight glass vials.
- J. Samples to be archived are documented on a spreadsheet and transferred to the CHL sample archive vault.

Archive System:

1. A request that a sample be archived is made by the scientist using the Request for Analysis form received by the lab manager and approved by the project leader.
2. Each sample is labeled with the sample information (ID, collection date, site sampled, amount, and principle investigator) is recorded on the sample archive sheet.
3. The sampling site, sample type, principle investigator and number of samples archived is recorded on the sample archive master list stored on the lab managers computer.
4. The sample is then placed in the archive building.
5. Plant tissue and soil samples are archived per scientist request, indefinitely.

The Archive Building is a stone building located next to the dorm. The interior has two separated rooms. Each room has a commercial refrigerator door. The floor between the rooms is made of concrete. The rooms are constructed on all sides (walls, floor and ceiling) of wood. The interior is always cool.

III. Laboratory Water Quality

Samples at CHL are characterized by very low concentrations of nutrients. The mean concentration for NO₃-N in a control watershed in 1992 was 6µg/L. The need for quality water cannot be overstated.

Deionized Water –A Millipore Milli-Q Integral system is used to give two types of water: Type I (ultra-pure) and Type II which meet or exceed standards set by the American Society of Testing and Materials. The system has a 200-liter storage tank that uses UV to eliminate biological activity in the tank. The Ultra-pure water produced by the Milli-Q is monitored by the DI system and maintains a resistivity of 18.2 megaohm cm. Type II has a resistivity of > 5 megaohm cm. Type II water is monitored through conductivity and pH checks by a lab technician and is documented on the quality assurance spreadsheet. The conductivity of type II water should not exceed 1µS cm⁻¹.

IV. Labware

A. Glass and Plastic Ware: Sample containers

1. Polypropylene bottles, 15ml and 50ml polypropylene tubes are used for water sample collection and storage. See [Appendix C](#) for required containers, preservation techniques and maximum Shelf Life for a number of parameters.
2. Lab personnel should be familiar with glassware limitations. Graduated cylinders are labeled TC or TD, to contain or to draw. This means liquid left behind in a cylinder labeled TC is part of the volume. The volume from cylinders labeled TD is not dependent on what is left behind. Volumetrics' differ in accuracy. A red line volumetric is most accurate and therefore is used for calibration standards and QC standard preparation.
3. Sample containers are discarded if cracks or inside scratches are present. All sample tubes

are discarded after one-year use.

B. Washing protocol

1. All labware is washed using Liqui-Nox[®], rinsed 5 times with tap water and rinsed 5 times using Type II DI water.
2. Some vials, glassware and sample tubes are rinsed in acid solution. See [Procedures for Chemical Analysis](#) (USDA FS Coweeta Hydrologic Laboratory 2017), **Washing of Glassware and Bottles** under **Laboratory Protocol** for further information.

V. **Quality Control Standards, Reagents, Solvents, Acids, and Bases**

A. Quality Control and Calibration Standards

1. Certified quality control (QC) standards are purchased from NSI solutions, Environmental Resource Associates (ERA) or a reputable company and are run on all instruments quarterly. The acceptable range is given by the manufacturer.
2. Reference standards are certified standards purchased from reputable commercial vendors such as National Institute of Standards and Technology (NIST).
3. Calibration standards are made up using good laboratory practices from certified stock standards using Type I DI water. QC standards are used to verify calibration curves. Calibrants are evaluated quarterly using NSI certified quality control standards or certified standards purchased from a reputable vendor.

B. Chemical Materials

1. The quality of the material must coincide with procedure needs, i.e. ICP work must have spectral grade. For most other applications, analytical grade reagents, solvents, acids, and bases are purchased.
2. An inventory spreadsheet is available on the lab manager's computer. The inventory spreadsheet identifies all chemicals used at CHL.
3. All containers are marked with date received and date opened. These are included on the inventory spreadsheet along with date of expiration, vendor, and storage requirements. The inventory spreadsheet includes the method for responsible disposal for expired material. This sheet is checked yearly by the lab manager.

VI. **Procedure for Quarterly Quality Control and Method Detection Limit Analysis**

- A. When QC samples arrive from the vendor, the certified values are entered on the quarterly QC spreadsheet, located on the lab manager's computer. Each instrument has a page in the spreadsheet containing calculated values for dilution. The diluted QC sample concentrations closely resembles CHL stream chemistry for all comparisons.
- B. Each analyst makes up a stock solution per the manufacturer's instructions. Subsequent dilutions are made from the stock.
- C. All stock solutions and dilutions are made using a red line volumetric and Type I DI water.
- D. If values fall outside the range, the analyst reruns the samples and if still a problem, remakes the QC's.
- E. If the values are still outside the range the lab manager is informed.
- F. The method detection limit is determined quarterly following EPA guidelines (USEPA 2016).

VII. Chemical Analyses

- A. Approved procedures of analysis are documented in the [*Procedures for Chemical Analysis*](#) (USDA FS Coweeta Hydrologic Laboratory 2017). *Procedures for Chemical Analysis* is updated as needed by the lab manager.
- B. All analysis performed on an instrument require a standard curve using approved calibrants. The correlation coefficient for the calibration curve must be 99% or better. A quality control sample is used to verify the curve and is included in the run as specified by the method. The QC sample must fall within the established range. If the value falls outside the range the data are unacceptable. The problem is isolated and corrected before continuing. Samples are rerun to the point where the problem occurred.
- C. Three reference samples plus three blanks are included in every extraction and digestion. The percent error allowed for a reference sample is specified by the manufacturer. If the value falls outside this range the data are unacceptable. The problem is isolated and corrected before continuing. Samples are rerun to the point where the problem occurred.
- D. The matrix of the calibration standards, reference standard and blanks used in a run match the matrix of the sample; unless it has been determined the analysis is not affected by the matrix.
- E. Dilutions
 1. Automatic pipettes are checked quarterly and logged on the quality assurance spreadsheet.
 2. All dilutions made by hand are done in duplicate and must agree within 10%.
- F. Modifications to a procedure in the [*Procedures for Chemical Analysis*](#) require the following:
 1. The new procedure and old procedure must be run using the same samples. If the new procedure requires use of a different instrument, follow the procedure for New Instrument in section XII E below. For extractions and or digestions: The same sample should be used for both procedures. This must be done for all sample matrices used with the procedure.
 2. The results are compared and if R^2 is not 0.95 or greater with a slope of 1, then a correlation factor is developed using regression analysis. All subsequent data is then corrected to a single procedure using the correlation equation.
 3. Modifications to a procedure require the approval of the Laboratory Quality Assurance Officer.
- G. New procedures should be tested to include correlation with other methods. The Project leader must approve any new procedure.
- H. After approval of a modified method or acceptance of a new method the lab manager updates the [*Procedures for Chemical Analysis*](#).
- I. New Sample Studies

New sample sets require verification the proper procedure is used for all conditions that affect the matrix of the sample. The following apply:

 1. The Laboratory Quality Assurance Officer determines if there is a matrix problem using the method of standard additions, spiked sample, or another instrument type when available.
 2. If a change in procedure of analysis is required, then the following applies:
 - a. The Laboratory Quality Assurance Officer develops new procedure for the sample set.
 - b. The new procedure, including a report explaining the problem and data comparisons, is sent to the Project leader for approval.

- c. The lab manager receives the new procedure for the cookbook.
3. The lab manager has the primary investigator sign off on the first sample set analyzed.

VIII. Trouble Shooting Problem with Analysis

When a problem with an analysis occurs (such as a matrix problem) then a procedure to identify and fix the problem must be established. This entails first isolation of questionable data and then development of a new procedure of analysis to deal with the samples. The lab manager determines the analysis to be undertaken. This should include analysis to justify the procedure such as the method of standard additions or samples run on an appropriate instrument such as the IC for comparison with the AutoAnalyzer.

When data/analysis problems are realized the following steps are taken:

1. Notify the Laboratory Quality Assurance Officer.
2. The Laboratory Quality Assurance Officer isolates the samples and data in question.
3. The Laboratory Quality Assurance Officer develops a new procedure for the sample set, either through preparation or analysis.
4. The new procedure including a report explaining the problem and data comparisons is sent to the project leader for approval.
5. The lab manager receives the new procedure for the cookbook.
6. Disposition of questionable data is made by the Project leader.

IX. Blanks

Analytical blanks or experimental blanks are included in all procedures for extracted and digested samples. A DI blank is included in the weekly Dryfall Collector analysis.

X. Blind samples

Principle investigators are encouraged to include blind checks, duplicates, and blanks with their samples. The lab manager should present blind samples for analysis to each analyst quarterly.

XI. Analysts, training

The lab manager or a qualified CHL technician trains new laboratory staff. The lab manager or CHL technician work closely with that person until he/she becomes proficient with an analysis and/or instrument.

XII. Instrumentation

A. Maintenance

1. Each instrument analyst carries out routine maintenance and records this information in a logbook.
2. All logbook maintenance information is transferred to a spreadsheet located on the lab manager's computer.
3. Laboratory balances are professionally cleaned and calibrated once a year by a qualified outside technician.

- B. Quarterly quality control checks are made on each instrument using purchased certified quality control standards. The results are recorded on the quality control spreadsheet. The information for each calibration curve is included on the quality Control spreadsheet. The**

percent error for each instrument is found in [Appendix D](#) at the end of this document. The vendor certifying the quality control sample has a certified value and a range associated with that value. This range is the allowable percent error. These values are based on actual historical data collected by the vendor. The range reflects any bias in the method used to establish the limits and closely approximate a 95% confidence interval of the performance that experienced laboratories should achieve using acceptable environmental methods. If results are outside of the allowable error, then the cause is documented and resolved before more data is collected. Results obtained between the current Quarterly check and the previous Quarterly check is scrutinized and inferior data is reported to the Laboratory Quality Assurance Officer for disposition. A yearly graph of quarterly results is documented to assess performance.

- C. Instrument background noise is evaluated during each run.
- D. Lower limits of detection, instrument detection limit and method detection limits are defined for each instrument in the [Procedures for Chemical Analysis](#) (USDA FS Coweeta Hydrologic Laboratory 2017). Methods Detection Limits can be found in [Appendix E](#) in this document.
- E. New Instrument

When a new instrument is purchased, the instrument accuracy, precision and stability must be determined. Before the old model is replaced the following is run on both instruments:

1. Run quarterly quality control.
2. After passing the above, run all sample types on both instruments for comparison.
3. The data is then reviewed by the Laboratory Quality Assurance Officer to replace the old instrument with the new instrument.

XIII. Data Storage and Reporting

- A. Significant figures are defined to three significant figures except for pH and sample weights for CN analysis of soil and plant tissue. These are defined to two places.
- B. Below the detection limit values and less than zero designations should not be substituted for the actual value. Actual results obtained including negative numbers should be recorded. See Waite et al. (1979) and Gilbert and Kinnison (1981) for techniques in averaging data sets containing the above. Each investigator must determine the appropriate method for those data.
- C. Permanent records are maintained for each instrument in a logbook, which include:
 1. Date samples were run, data file ID, and samples ID.
 2. Routine maintenance and major service repairs.
 3. Unusual occurrences during the run.
 4. Logbook information containing maintenance checks, instrument problems and service repairs are entered on the Sample Count Spreadsheet located on the lab managers computer.
- D. Disposition of data
 1. The data is examined by the analyst before being entered onto the main computer to ensure calibrants and QC values are within the specified controls.
 2. After entering data on the appropriate work sheet each analyst checks to ensure data is reasonable and agrees with historical data: Some spreadsheets contain conditional formatting for historical values of the sample. Conditional formatting gives the value in red rather than black if the value is outside historical data values. The analyst should then rerun that sample. If all values are red or out of the range from historical values, then a

problem could exist and must be evaluated. If it is determined the data is questionable then the procedure outlined in troubleshooting problems with analysis is used.

3. After all analyses have been run, the lab manager checks the data for anomalies and errors. Once checked the data is copied to the appropriate folder. The data in this folder is then ready for use outside the lab.
- D. Data files sent to the lab manager's computer are backed up monthly on a backup drive. These files are stored on the NAS.
 - E. The Meta Data associated with the analysis is attached with all data sent out. Meta data includes procedure of analysis, method detection limit, and information regarding the instrument used in the analysis (model, manufacturer and instrument in operation date).

XIV. Facilities

- A. Heating, cooling ventilation and utilities are maintained to provide a consistent controllable environment.
- B. Electricity, compressed gasses and water are of appropriate quality to meet QC standards.
- C. Laboratory Cleanliness
 1. Soils, litter and forest floor samples should be weighed in the soil lab or back room.
 2. All floor areas should be swept following sampling preparation.
 3. Balances, lab bench tops and hoods should be kept free of chemicals. All chemical spills should be cleaned immediately.
 4. Because fixtures such as lights, spigots and air taps corrode they should be checked yearly.
- D. See [Coweeta Hydrologic Laboratory Lab Safety Manual](#) for more info.

XV. Waste Disposal

All chemical waste, batteries, lamps, and electronic equipment are disposed of following state and federal guidelines.

References

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Appendix A

Coweeta Analytical Lab - REQUEST FOR ANALYTICAL SERVICES

Please send the completed form to Lab Manager Cindi Brown – <mailto:cindi.l.brown@usda.gov>

Name of Study _____
 Principle Investigator _____
 Date(s) Sampling Initiated _____
 Type of sample (i.e. Water, Soil, Plant) _____

Number of samples per collection _____
 Number of Collections and Frequency _____
 Sample ID's (Must include) _____

Study Duration (ex - 1 yr, 1 time, quarterly) _____
 Archive Sample (plant and soil only) _____
 Project Leader Approval _____

Check beside each desired analysis*:

Water	Soil	Plant Tissue
DOC/TN	SOIL EXTRACTIONS:	TOTAL CATIONS
NO₃-N	1) KCL	CN
NH₄-N	NO₃-N	
SO₄	NH₄-N	
Cl	2) DBL. ACID	
SiO₂	Cations	
O-PO₄	P – soluble P	
K	3) NH₄CL:	
Na	Cations	
Ca	Al	
Mg	CEC	
Al	4) Phosphate extract	
pH (must be analyzed day collected)	SO₄	
HCO₃ (must be analyzed day collected)	TOTAL CATIONS	
TOTAL P (by ICP analysis)	Total Organic P	
CONDUCTIVITY (must be analyzed day collected)	SOIL pH	
	Exchangeable Acidity	
	CN	

*For information on sample preparation and analytical methods refer to:
 “Coweeta Analytical Lab Cookbook:: [Procedures for Chemical Analysis](#)
 “Standard Methods for the Examination of Water”

Consult with Cindi Brown – Lab Manager

Notes:

Appendix B –Shelf Life

The maximum amount of time a sample may be stored between collection and analysis is referred to as the shelf life (or holding time). Samples analyzed past the shelf life are compromised and may be considered invalid, depending on the target analytes and the intended use of the data. The target analytes may have been lost due to volatilization, chemical or microbial degradation, or other processes. In order to retard these processes, certain analytes require chemical preservation and/or cooling. In order to preserve samples, the preservative should be added to the sample container prior to, or at, the time of collection.

Shelf Life¹

**	SO ₄	o-PO ₄	TP*	NO ₃	Cl	Br	NH ₄	SiO ₂	K	Na	Ca	Mg	DOC	TN	pH
H₂O	5 days	2 days	2 days	2 days	5 days	28 days	2 days	28 days	2 weeks	2 weeks	2 weeks	2 weeks	5 days	5 days	Immediately
NH₄Cl	na	na	na	na	na	na	na	na	5 days	5 days	5 days	5 days	na	na	na
KCl	na	na	na	4 weeks	na	na	4 weeks	na	na	na	na	na	na	na	na
NH₄OAc	na	na	na	na	na	na	na	na	5 days	5 days	5 days	5 days	na	na	na
2% HNO₃	na	6 months	na	na	na	na	na	na	6 months	6 months	6 months	6 months	na	na	na
Double acid	na	<5 days	na	na	na	na	na	na	<5 days	<5 days	<5 days	<5 days	na	na	na
Bray	na	na	<5 days	na	na	na	na	na	na	na	na	na	na	na	na

*Note: acidified samples for TP have a 28-day shelf life

** Some samples can be frozen and run at a later date. Check with lab manager.

1. Environmental Protection Agency, Code of Federal Regulations, 40CFR 136.3,(revised 2002).

Rain gauge bottles receive the addition of 1ml of PMA solution as a preservative. See [Procedures for Chemical Analysis](#), page 4 for further information.

Appendix C - Required Containers, Preservation Techniques, and Shelf Life¹

Shaded gray areas indicate currently tested at Coweeta Hydrologic Laboratory

Parameter No./name	Container ¹	Preservation ^{2,3}	Maximum holding time ⁴
Table IA—Bacteria Tests:			
1–4 Coliform, fecal and total	P, G	Cool, 4C, 0.008% Na ₂ S ₂ O ₃ ⁵	6 hours.
5 Fecal streptococci	P, G	Cool, 4C, 0.008% Na ₂ S ₂ O ₃ ⁵	6 hours.
Table IA—Aquatic Toxicity Tests:			
6–10 Toxicity, acute and chronic	P, G	Cool, 4 °C ¹⁶	36 hours.
Table IB—Inorganic Tests:			
1. Acidity	P, G	Cool, 4°C	14 days.
2. Alkalinity	P, G	do	Do.
4. Ammonia	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
9. Biochemical oxygen demand	P, G	Cool, 4°C	48 hours.
10. Boron	P, PFTE, or Quartz.	HNO ₃ TO pH<2	6 months.
11. Bromide	P, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours.
15. Chemical oxygen demand	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
16. Chloride	P, G	None required	Do.
17. Chlorine, total residual	P, G	do	Analyze immediately.
21. Color	P, G	Cool, 4°C	48 hours.
23–24. Cyanide, total and amenable to chlorination.	P, G	Cool, 4°C, NaOH to pH>12, 0.6g ascorbic acid	14 days ⁶
25. Fluoride	P	None required	28 days.
27. Hardness	P, G	HNO ₃ to pH<2, H ₂ SO ₄ to pH<2	6 months.
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately.
31, 43. Kjeldahl and organic nitrogen	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
Metals: ⁷			
18. Chromium VI	P, G	Cool, 4°C	24 hours.
35. Mercury	P, G	HNO ₃ to pH<2	28 days.
3, 5–8, 12, 13, 19, 20, 22, 26, 29, 30, 32–34, 36, 37, 45, 47, 51, 52, 58–60, 62, 63, 70–72, 74,			
75. Metals, except boron, chromium VI and mercury.	P, G	do	6 months.
38. Nitrate	P, G	Cool, 4°C	48 hours.
39. Nitrate-nitrite	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
40. Nitrite	P, G	Cool, 4°C	48 hours.
41. Oil and grease	G	Cool to 4°C, HCl or H ₂ SO ₄ to pH<2	28 days.
42. Organic Carbon	P, G	Cool to 4 °C HCl or H ₂ SO ₄ or H ₃ PO ₄ , to pH<2.	28 days.
44. Orthophosphate	P, G	Filter immediately, Cool, 4°C	48 hours.
46. Oxygen, Dissolved Probe	G	Bottle and top. None required	Analyze immediately.
47. Winkler	do	Fix on site and store in dark	8 hours.
48. Phenols	G only	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
49. Phosphorus (elemental)	G	Cool, 4°C	48 hours.
50. Phosphorus, total	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
53. Residue, total	P, G	Cool, 4°C	7 days.
54. Residue, Filterable	P, G	do	7 days.
55. Residue, Nonfilterable (TSS)	P, G	do	7 days.
56. Residue, Settleable	G	do	48 hours.
57. Residue, volatile	P, G	do	7 days.
61. Silica	P, PFTE, or Quartz.	Cool, 4 °C	28 days.
64. Specific conductance	P, G	do	Do.
65. Sulfate	P, G	do	Do.
66. Sulfide	P, G	Cool, 4°C add zinc acetate plus sodium hydroxide to pH>9	7 days.
67. Sulfite	P, G	None required	Analyze immediately.
68. Surfactants	P, G	Cool, 4°C	48 hours.
69. Temperature	P, G	None required	Analyze.

73. Turbidity P, G Cool, 4 °C 48 hours.

Table IC—Organic Tests ⁸

13, 18–20, 22, 24–28, 34–37, 39–43, 45–47, 56,

76, 104, 105, 108–111, 113. Purgeable Halocarbons. G, Teflonlined septum. Cool, 4 °C, 0.008% Na₂S₂O₃.⁵ 14 days.

6, 57, 106. Purgeable aromatic hydrocarbonsdo Cool, 4 °C, 0.008% Na₂S₂O₃,⁵ HCl to pH² ⁹. Do.

3, 4. Acrolein and acrylonitriledo Cool, 4 °C, 0.008% Na₂S₂O₃,⁵ adjust pH to 4–5¹⁰ Do.

23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 112. Phenols¹¹. G, Teflonlined cap. Cool, 4 °C, 0.008% Na₂S₂O₃.⁵ 7 days until extraction; 40 days after extraction.

7, 38. Benzidines ¹¹dodo 7 days until extraction.¹³

14, 17, 48, 50–52. Phthalate esters ¹¹do Cool, 4 °C 7 days until extraction; 40 days after extraction.

82–84. Nitrosamines ^{11,14}do Cool, 4 °C, 0.008% Na₂S₂O₃,⁵ store in dark. Do.

88–94. PCBs ¹¹do Cool, 4 °C Do.

54, 55, 75, 79. Nitroaromatics and isophorone ¹¹ ..do Cool, 4 °C, 0.008% Na₂S₂O₃,⁵ store in dark. Do.

1, 2, 5, 8–12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear aromatic hydrocarbons ¹¹dodo Do.

15, 16, 21, 31, 87. Haloethers ¹¹do Cool, 4 °C, 0.008% Na₂S₂O₃.⁵ Do.

29, 35–37, 63–65, 73, 107. Chlorinated hydrocarbons ¹¹do Cool, 4 °C Do.

60–62, 66–72, 85, 86, 95–97, 102, 103. CDDs/CDFs ¹¹ aqueous: field and lab preservation. .. G Cool, 0–4 °C, pH < 9, 0.008% Na₂S₂O₃. 1 year.

Solids, mixed phase, and tissue: field preservationdo Cool, < 4 °C 7 days.

Solids, mixed phase, and tissue: lab preservationdo Freeze, < -10 °C 1 year.

Table ID—Pesticides Tests:

1–70. Pesticides ¹¹do Cool, 4 °C, pH 5–9 ¹⁵ Do.

Table IE—Radiological Tests:

1–5. Alpha, beta and radium P, G HNO₃ to pH < 2 6 months.

Appendix C-- Notes

1. Polyethylene (P) or glass (G). For microbiology, plastic sample containers must be made of sterilizable materials (polypropylene or other autoclavable plastic).

2. Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4 °C until compositing and sample splitting is completed.

3. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

4. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional Administrator under § 136.3(e). Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See § 136.3(e) for details. The term “analyze immediately” usually means within 15 minutes or less of sample collection.

5. Should only be used in the presence of residual chlorine.

6. Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

7. Samples should be filtered immediately on-site before adding preservative for dissolved metals.

8. Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.
9. Sample receiving no pH adjustment must be analyzed within seven days of sampling.
10. The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.
11. When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum Shelf Life should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6–9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).
12. If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.
13. Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.
14. For the analysis of diphenylnitrosamine, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ and adjust pH to 7–10 with NaOH within 24 hours of sampling.
15. The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$.
16. Sufficient ice should be placed with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, it is necessary to immediately measure the temperature of the samples and confirm that the 4C temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature can not be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature.

Appendix D

Allowable Percent Error by Vendor of Certified Standards

<u>Method Instrument</u>	<u>Analyte</u>	<u>Allowable ±% Error¹</u>	<u>Found average Absolute %Error²</u>	<u>Found average %RSD²</u>
ICP-OES	K	15	7.81	0.58
ICP-OES	Na	15	6.15	1.48
ICP-OES	Ca	14	4.55	2.07
ICP-OES	Mg	14	5.49	0.98
ICP-OES	P	19	3.69	1.71
ICP-OES	Al	21	11.92	0.61
Auto Analyzer	NH ₄	16	4.80	1.37
Auto Analyzer	NH ₄ soil	16	4.68	1.97
Auto Analyzer	NO ₃ soil	10	5.12	0.70
Auto Analyzer	SiO ₂	15	9.58	0.70
Auto Analyzer	PO ₄ soil	14	2.50	2.51
Ion Chromatography	Cl	10	4.09	1.71
Ion Chromatography	NO ₃	10	4.33	1.64
Ion Chromatography	PO ₄	10	3.98	1.96
Ion Chromatography	SO ₄	10	4.79	1.13
Ion Chromatography	Br	10	6.01	3.59
Ion Chromatography	F	10	6.40	6.40
TOC analyzer	DOC	17	4.23	1.04
TN analyzer	TN	23	2.09	3.42
pH meter	pH	2.4	0.39	0.04

1. The vendor certifying the quality control sample has a certified value and a range associated with that value. This range is the allowable percent error. The ranges are based on actual historical data collected by the vendor. The range reflects any bias in the method used to establish the limits and closely approximate a 95% confidence interval of the performance that experienced laboratories should achieve using acceptable environmental methods.

2. %Absolute Accuracy and %RSD are the result of analysis in 2017 for Quarterly QC values for CHL.

Appendix E - Method Detection Limits (mdl), by Sample Type - Method detection limit for 10 observations at 99% confidence level (USEPA 2016)

Water

Analyte	Lab Designation	Method	Instrument	Instrument in Operation	Units of reported values	mdl 2020 matrix=DI
Ammonium-Nitrogen	NH ₄ -N	automated Phenate method	Astoria 2 Autoanalyzer, Astoria-Pacific, Clackamas, Oregon	November 2015	mg/L	0.001
Silicate	SiO ₂	Ammonium Molybdate reaction and reduction with Ascorbic Acid	Astoria 2 Autoanalyzer, Astoria-Pacific, Astoria, Oregon	November 2015	mg/L	0.001
Potassium	K	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	mg/L	0.002
Sodium	Na	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	mg/L	0.001
Calcium	Ca	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	mg/L	0.010
Magnesium	Mg	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	mg/L	0.002
Total dissolved phosphorous	TDP	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	mg/L	0.003
Aluminum	Al	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	mg/L	0.004
Chloride	Cl	Micro-membrane Suppressed Ion Chromatography, using a capillary AS 18 column	Thermo Scientific ICS 4000 capillary Ion Chromatograph, from Dionex, Sunnyvale, CA	June 2014	mg/L	0.001
Bromide	Br	Micro-membrane Suppressed Ion Chromatography, using a capillary AS 18 column	Thermo Scientific ICS 4000 capillary Ion Chromatograph, from Dionex, Sunnyvale, CA	June 2014	mg/L	0.002

Water Continued

Analyte	Lab Designation	Method	Instrument	Instrument in Operation	Units of reported values	mdl 2020 matrix=DI
Nitrate-Nitrogen	NO ₃ -N	Micro-membrane Suppressed Ion Chromatography, using a capillary AS 18 column	Thermo Scientific ICS 4000 capillary Ion Chromatograph, from Dionex, Sunnyvale, CA	June 2014	mg/L	0.001
ortho Phosphate (Ortho-phosphate is sometimes referred to as "reactive phosphorus.")	PO ₄	Micro-membrane Suppressed Ion Chromatography, using a capillary AS 18 column	Thermo Scientific ICS4000 capillary Ion Chromatograph, from Dionex, Sunnyvale, CA	June 2014	mg/L	0.003
Sulfate	SO ₄	Micro-membrane Suppressed Ion Chromatography, using a capillary AS 18 column	Thermo Scientific ICS4000 capillary Ion Chromatograph, from Dionex, Sunnyvale, CA	June 2014	mg/L	0.003
Fluoride	F	Micro-membrane Suppressed Ion Chromatography, using a capillary AS 18 column	Thermo Scientific ICS4000 capillary Ion Chromatograph, from Dionex, Sunnyvale, CA	June 2014	mg/L	0.003
Dissolved organic carbon	DOC	catalytically-aided platinum 680°C combustion technique for sample oxidation	Shimadzu DOC-VCPHTNM-1 analyzer, Shimadzu Scientific Instruments, Columbus, MD	November 2016	mg/L	0.046
Total dissolved nitrogen	TDN	luminescence	Shimadzu DOC-VCPHTNM-1 analyzer, Shimadzu Scientific Instruments, Columbus, MD	November 2016	mg/L	0.013
Hydrogen ion activity in in water	pH for Water	Standard Methods using a Broadley James pH combo probe, Broadley James Corp, Irvine CA	Thermo Scientific Orion A211 pH benchtop	Sept 2015	pH units	0.013
HCO ₃ as CaCO ₃	BiCarbonate ANC	titration	Thermo Scientific Orion A211 pH benchtop		mg/L	0.655
Conductivity	Conductivity		YSI 3100	2012	uS	0.431

Soil

Analyte	Lab Designation	Method	Instrument	Instrument in Operation	matrix	Units of reported values	mdl 2020
Ammonium-Nitrogen	NH ₄ -N	automated Phenate method	Astoria 2 Autoanalyzer, Astoria-Pacific, Clackamas, Oregon	November 2015	2N KCl	mg/L	0.008 (2019)
Nitrate-Nitrogen	NO ₃ -N	reduction using a cadmium coil	Astoria 2 Autoanalyzer, Astoria-Pacific, Astoria, Oregon	November 2015	2N KCl	mg/L	0.003 (2019)
ortho Phosphate (Orthophosphate is sometimes referred to as "reactive phosphorus.")	PO ₄	Ammonium Molybdate /Antimony Potassium Tartrate reaction and reduction with Ascorbic Acid	Astoria 2 Autoanalyzer, Astoria-Pacific, Clackamas, Oregon	November 2015	2N KCl	mg/L	0.005 (2018)
Potassium	K	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	1N NH ₄ Cl	mg/L	0.158
Sodium	Na	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	1N NH ₄ Cl	mg/L	0.039
Calcium	Ca	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	1N NH ₄ Cl	mg/L	0.080
Magnesium	Mg	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	1N NH ₄ Cl	mg/L	0.032
Aluminum	Al	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	1N NH ₄ Cl	mg/L	0.049
carbon	C (soil)	dumas method	Thermo Scientific Flash EA 1112 NC analyzer, CE Elantech, Lakewood, NJ	9/15/05	Santis CNSsoil reference	%	0.398
nitrogen	N (soil)	dumas method	Thermo Scientific Flash EA 1112 NC analyzer, CE Elantech, Lakewood, NJ	9/15/05	Santis CNSsoil reference	%	.044
Hydrogen ion activity in water	pH for soil	Standard Methods using an Orion 9165N combination pH combo probe, Broadley James Corp, Irvine CA	Thermo Scientific Orion 3Star pH benchtop	Sept 2015	0.01M CaCl ₂	pH units	0.010 (2019)

Plant

Analyte	Lab Designation	Method	Instrument	Instrument in Operation	matrix	Units of reported values	2020
Potassium	K	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	2%HNO ₃	mg/L	0.216
Sodium	Na	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	2%HNO ₃	mg/L	0.115
Calcium	Ca	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	2%HNO ₃	mg/L	0.160
Magnesium	Mg	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	2%HNO ₃	mg/L	0.174
phosphorous	P	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	2%HNO ₃	mg/L	0.174
Aluminum	Al	Optical Emission	Thermo Fisher iCAP 6300, Madison WI	November 2012	2%HNO ₃	mg/L	0.183
carbon	C (plant)	dumas method	Thermo Scientific Flash EA 1112 NC analyzer, CE Elantech, Lakewood, NJ	9/15/05	NIST 1573a	%	0.397
nitrogen	N (plant)	dumas method	Thermo Scientific Flash EA 1112 NC analyzer, CE Elantech, Lakewood, NJ	9/15/05	NIST 1573a	%	0.086

NIST – National Institute of Standards and Technology