Appendix 6: Laboratory Section QA Information

Quality Assurance Manual for the North Carolina Division of Water Quality Laboratory Section, June 2015

North Carolina Division of Water Resources

Quality Assurance Manual for the North Carolina Division of Water Resources Water Sciences Section Chemistry Laboratories

Original Adopted November 2004

Revision 1 June 30, 2015

Quality Assurance Manual

for the

North Carolina Division of Water Resources

Water Sciences Section Chemistry Laboratories

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1.0 Review-Tracking Form

Revision Number	Revision Date	Revision Summary
1	06/30/15	Revised division and section names
1	06/30/15	Updated laboratory program names and unit names
1	06/30/15	References to Washington Regional Office Laboratory were removed.
1	06/30/15	Star LIMs was replaced with Labworks™ throughout document. Update of Login process with Labworks™ was added. Section 7.0
1	04/01/5	References to Laserfiche® were added throughout document.
1	06/30/15	Revised Table of Contents Section 2.0
1	06/30/15	Added review tracking form
1	06/30/15	Central Laboratory Major Equipment List was removed from the QAM.
1	06/30/15	Updated NC DENR mission statement. Section 1.0
1	06/30/15	Updated DWR WSS Laboratory positions, responsibilities and organizational chart. Section 4.0
1	06/30/15	Updated Safety Orientation and Training documents. Section 4.0
1	06/30/15	Added Certification Modular Building Schematic. Section 4.0
1	06/30/15	Updated Table 5.1 - 5.10 EXAMPLES of QA Targets for Accuracy, Precision and MDLs/PQLs. Section 5.0
1	06/30/15	Bottle testing procedure was added to Section 6.0
1	06/30/15	Updated Lab Reagent Water .Section 8.6, QC protocol and Table 9.1 Calibration Frequency, Procedures, Standards, and Acceptance Criteria for Support Equipment. Section 9.0
1	06/30/15	Update Table 10.1 Laboratory Equipment Preventive Maintenance Schedule. Section 10
1	06/30/15	Updated preservation tables (Tables 6.1 and 6.2) documents content to reflect 40 CFR 136 2012 Method Rule Update. Section 6.0
1	06/30/15	Added memo dated 10/13/2013 from S. Jay Zimmerman, P.G. to Aquifer Protection Section Supervisors. Subject: Aquifer Protection Section Policy for Metals Determination Required by Title 15A, NC Administrative Code, Subchapter 21. Section 8.0
1	06/30/15	Removed memo dated 05/25/2001 to Steve Tedder Lab Section Chief in 2001 from Arthur Mouberry Ground Water Section Chief in 2001 Subject: Request to change Ground water Section's Metal Policy.
1	06/30/15	Updated Lab Report document. Section 12.0
1	06/30/15	Updated Sample Condition Upon Receipt (SCUR) and Sample Anomaly (SAR) forms. Section 13.0
1	06/30/15	Added QA Semi-annual Report to Management format. Section15.0
1	06/30/15	Added Access Record File to section 3.3 and revised Confidentiality of section 3.1
1	06/30/15	Updated DWR WSS and Asheville Regional Office ,Added Underground Storage Tank WQ Sediment,Soil and Tissue Field sheets Section 7.0
1	06/30/15	Added U.S. EPA Memorandum Recommended Approved Modification to EPA 625. Section 8.0
1	06/30/15	Added Corrective Action Report (CAR) Form as Appendix I
1	06/30/15	Revised Qualifier codes A & V.,PQL definition and added Minimum Level and Method Detection Limit definitions Section 12.3.1
1	06/30/15	Added Qualifier Codes as Appendix II
1	06/30/15	Old Safety Orientation and Training documents as Appendix III
1	06/30/15	Added DWR WSS Laboratory Data Retention Policy as Appendix IV
1	06/30/15	Updated QC protocol in section 9.0
1	06/30/15	Added Nexion-350 and calibration information to Section 9.
1	06/30/15	Added Section 17 to indicate where Appendices begin
1	06/30/15	Editorial Revisions
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Disclaimer
The mention of trade names or commercial products in this manual is for illustration purposes only and does not constitute endorsement or recommendation for use by the DWR.

2.0 Table of Contents

3.0 Statement of Policy

It is the mission of the North Carolina Department of Environment and Natural Resources (NCDENR) to provide leadership, education and advocacy for the responsible stewardship of North Carolina's environment and natural resources. It is recognized that the N.C. Department of Environment and Natural Resources' primary mission is to protect North Carolina's environment and natural resources

The mission of the Water Sciences Section is to provide the Division with accurate information pertaining to waters of the state. Excellent service along with water quality monitoring and certification programs and analytical laboratory analyses that provide scientifically defensible data are the section's main avenues for accomplishing this mission. These activities support the management and protection of North Carolina's water resources for the health and welfare of the citizens of North Carolina and the economic well-being of the state.

The Water Sciences Section provides analytical and technical support to the divisions and programs within the Department of Environment and Natural Resources. To ensure that the results produced and reported meet the requirements of the data users and comply with state and federal regulations, a quality management system has been implemented that is clear, effective, well-communicated, and supported at all levels of the Division. The Quality Assurance Manual (QAM) details the quality assurance (QA) program in effect at the DWR laboratories. The primary purpose of this document is to establish and maintain uniform operational and quality control procedures and to ensure data is of a known and documented quality.

A well-conceived QA program provides a sound framework for the generation of laboratory data that is scientifically valid, representative and legally defensible. The validity and reliability of the data generated by the Water Sciences Section are assured by adherence to rigorous quality assurance/quality control (QA/QC) protocols. The application of sound QA/QC principles, beginning with initial planning and continuing through all field and laboratory activities, including the final report, are designed to meet that goal. The fundamental elements of the Water Sciences Section's QA program include Standard Operating Procedures (SOPs), quality control practices, performance testing samples, internal audits, external audits and an ethics policy.

This manual and the quality control procedures described within are not to be viewed as complete. Rather, they serve as a basic foundation on which to build a stronger, more viable Quality Assurance Management Plan (QAMP) within the Section. Other documents that may detail or affect the quality management program include the Chemical Hygiene Plan (CHP), quality guidance documents, memoranda, work instructions, standard operating procedures and periodic reports. These documents may further define or guide the implementation of quality standards within the Water Sciences Section, but shall not conflict with the QAMP or diminish the effectiveness of the program. Adherence to the practices described in this manual is required of all employees.

All employees are required to familiarize themselves with the sections of this manual that pertain to their operations and are encouraged to comment on its contents and make recommendations for more efficient procedures. The QAM when revised is printed and a hard copy presented to each unit as well as and electronic copy placed on the server for employee access. Each employee is asked to read the QAM and, upon completion, submit to their unit supervisor a signed email stating that they have read and understand the QAM.

Following is a list of documents used to develop the Water Sciences Section Chemistry Laboratory's QAMP:

- EPA Requirements for Quality Management Plans, U.S. Environmental Protection Agency, EPA QA/R-2, March 2001, *et seq*.
- EPA Requirements for Quality Assurance Project Plans, USEPA QA/R-5, *et seq*.
- Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs, American Society for Quality Control, Energy and Environmental Quality Division, Environmental Issues Group, ANSI/ASQC E4-1994 (Formerly EQA-1), January 1994, *et seq*.
- Quality Management and Quality System Elements for Laboratories - Guidelines, American National Standard, American Society for Quality Control, ANSI/ASQC Q2-1991, *et seq*.
- The North Carolina Administrative Code, 15A NCAC 2H .0800, governing Laboratory Certification.

3.1 Analytical Laboratory Services

The DWR Water Sciences Section Chemistry Laboratory is a technical support organization with the following functions:

- Provides analytical laboratory support to the Department of Environment and Natural Resources in the form of physical and chemical analyses of surface water, wastewater, groundwater, soil, sediment and fish tissue samples.
- Provides consultation and assistance to state and local agencies, private laboratories and individuals in matters of analytical methodology and quality assurance.
- Operates a laboratory certification program to control the quality of state-required monitoring analysis.

The North Carolina Division of Water Resources' Water Sciences Section Chemistry Laboratories provide chemical, physical and microbiological analyses of surface water, groundwater, sediment, fish tissue and spill samples from around the state for the Division of Water Resources' Water Quality Section and the Division of Waste Management. The Quality Assurance/Quality Control (QA/QC) office is responsible for establishing, implementing and coordinating a comprehensive QA/QC program for environmental sampling and analyses performed by the North Carolina Division of Water Resources Water Sciences Section. The QA/QC office is dedicated to ensuring that environmental data operations are of a quality that meet or exceed requirements for informed decision making. This office is responsible for providing information, guidance and expertise in quality control and regulatory compliance issues to ensure the laboratories of the Water Sciences Section adhere to standards that meet federal and state monitoring requirements allowing for appropriate decisions to be made to protect human health and the environment. Analytical results produced by the laboratories are utilized by a variety of state and federal agencies including the NC Division of Water Resources, NC Division of Waste Management, NC Division of Marine Fisheries, NC Department of Health and Human Services, municipal governments, USEPA, and US Centers for Disease Control.

3.2 Ethics

All employees of the DWR Water Sciences Section are held to high professional ethical standards in the performance of their duties. All employees are required to read, understand and sign a 'Code of Ethics Statement' (Figure 3.1) attesting to their commitment to honesty and integrity in discharging their public duties. A copy of this document is retained in the employee's Training Documentation File. Improper, unethical or illegal actions will be dealt with according to the published Administrative Directives of the State Personnel Manual (Section 7.0) which contains the policies, regulations and procedures of the Office of State Personnel that apply to employees covered by the State Personnel Act.

Unethical activities are defined as intentional falsification of records. Records may be personal credentials, resumes or educational transcripts, instrument logbooks, maintenance logbooks, raw data and data reports. *Scientific misconduct* is defined as intentionally not adhering to the prescribed method or Standard Operating Procedure. Falsifications in the environmental laboratory industry that the NC DWR Water Sciences Section will not tolerate include, but are not limited to:

- **Falsifying data** - This includes "dry-labbing", the process of making up/creating data without performing the procedure. This may also include intentionally representing another individual's work as one's own or changing laboratory data results.
- **Improper peak integration** - Intentionally integrating data chromatograms so that the quality control samples meet QC criteria. This is also known as "peak shaving" or "peak juicing".
- **Improper clock setting** - Readjusting the computer clock so that it appears samples were analyzed within hold times. This is also known as "time traveling".
- **Improper representation of quality control samples** - Misrepresenting analytical spikes as matrix (digested) spikes. Analyzing a blank or LCS without sending it through the preparatory procedure. Treating a QC sample differently than a client sample.
- **Improper calibration** - Manipulating the calibration or tune so that it meets QC criteria. Examples are deleting/discarding calibration points along a curve or forging tuning data so that it appears to have met calibration criteria.
- **File substitution** - Substituting invalid calibration data with valid data from a different time so that the analysis appears to be successful.
- **Hiding or concealing a problem** - Concealing a known analytical or sample problem as well as concealing a known ethical problem.

Such actions are considered personal conduct violations under State disciplinary policy. Disciplinary action for ethics violations may include verbal or written reprimand, reassignment, or termination depending on the number of infractions observed, the severity of the infraction, or the impact it may cause to the environment and human health.

3.3 Confidentiality

All records and documents generated by the DWR Water Sciences Section, except those associated with active criminal investigations, are public records and may be subject to disclosure according to the guidelines and exceptions published in Chapter 132 of the North Carolina General Statutes. The DWR WSS Laboratory has the responsibility to the public to safeguard these records and to carry out our day-to-day program obligations. The staff of the Water Sciences Section Laboratory is dedicated to making public records in our custody readily available to the public for review and copying. The following guidelines must be followed when reviewing laboratory files.

The guidelines for reviewing laboratory files are presented on the File Access Record Form (Figure 3.2). The reviewer's name, identification of the files reviewed, analytical unit, date of review, signature of reviewer and whether any copies were made are documented on the File Access Log (File Access Record Form - Figure 3.2). These completed logs are maintained by the Quality Assurance Office

Figure 3.1. Code of Ethics Statement Form

NC DWR
Water Sciences Section
Code of Ethics Statement

I, the undersigned, CERTIFY that:

I have an ethical and legal responsibility to produce data that is accurate and defensible. I must conduct myself at all times in an honest and ethical manner.

I have read and reviewed the most current Quality Assurance Manual and will adhere to it in the strictest manner. I continually strive to improve the quality and service of my work.

I will promptly notify my Supervisor or Branch Manager of any problem that may slow down or limit my work productivity. I will promptly and efficiently resolve the problem prior to generating reportable data.

I understand that *unethical activities* are defined as intentional falsification of records. Records may be personal credentials, resumes or educational transcripts, instrument logbooks, maintenance logbooks, raw data and data reports. *Scientific misconduct* is defined as intentionally not adhering to the prescribed method or Standard Operating Procedure. Falsifications in the environmental laboratory industry that the NC DWR Water Sciences Section will not tolerate include, but are not limited to:

- **Falsifying data** - This includes "dry-labbing", the process of making up/creating data without performing the procedure. This may also include intentionally representing another individual's work as one's own or changing laboratory data results.
- **Improper peak integration** - Intentionally integrating data chromatograms so that the quality control samples meet QC criteria. This is also known as peak shaving or "peak juicing".
- **Improper clock setting** - Readjusting the computer clock so that it appears samples were analyzed within hold times. This is also known as time traveling.
- **Improper representation of quality control samples** - Misrepresenting analytical spikes as matrix (digested) spikes. Analyzing a blank or LCS without sending it through the preparatory procedure. Treating a QC sample differently than a client sample.
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- **File substitution** - Substituting invalid calibration data with valid data from a different time so that the analysis appears to be successful.
- **Hiding or concealing a problem** - Concealing a known analytical or sample problem as well as concealing a known ethical problem.

I agree to inform my direct line supervisor of any accidental reporting of non-authentic data by myself in a timely manner and I agree to inform my direct line supervisor of any accidental or intentional reporting of non-authentic data by other employees.

I know this policy will be strictly enforced and the NC DWR Water Sciences Section will not tolerate any unethical activities or scientific misconduct. Consequences of violating this Code of Ethics may lead to repercussions ranging from a severe reprimand to immediate termination, and depending on the situation, possible criminal prosecution.

_____ _____ _____/_____/_____
Employee Name Signature Initials Date

Figure 3.2. File Access Record Form

North Carolina Department of Environment and Natural Resources
Division of Water Resources
Water Sciences Section
Laboratory

FILE ACCESS RECORD

Guidelines for Access: The staff of the Water Sciences Section Laboratory is dedicated to making public records in our custody readily available to the public for review and copying. We also have the responsibility to the public to safeguard these records and to carry out our day-to-day program obligations. Please carefully read the following before signing the form.

1. We request that you call at least a day in advance to schedule an appointment for file review so you can be accommodated. Appointments will be scheduled Monday through Friday between 9:00 am and 3:00 pm. Viewing time ends at 4:40 pm. Anyone arriving without an appointment may view the files to the extent that time and staff supervision are available.
2. Please specify the files you want to review by sample number for laboratory files and Certification # or Laboratory Name for the Certification Program files. The number of files that you may review at one appointment may be limited due to time constraints.
3. You may make copies of a file when the copier is not in use by the staff and if time permits. The first 25 pages are free. Beyond 25 pages, the cost per copy is $0.05 cents per page, front and back will be $0.10 cents a sheet. Payment is to be made by check, money order, or cash in the administrative office.
4. FILES MUST BE KEPT IN THE ORDER YOU RECEIVED THEM. Files may NOT be taken from the office. No briefcases, large totes, etc. are permitted in the file review area. To remove, alter, deface, mutilate, or destroy material in one of these files is a misdemeanor for which you can be fined up to $500.00.
5. In accordance with General Statute 25-3-512, a $25.00 processing fee will be charged and collected for checks on which payment has been refused.
6. The customer must present a photo ID and sign-in prior to reviewing files.

File	Certification Number or Laboratory Unit for Lab Files	Laboratory Name for Certification Program or Sample Number for Laboratory Files	Copies Made YES / NO
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			

Name [please print]: _____ Date: _____

Signature: _____

4.0 Organization, Facilities and Equipment

The Water Sciences Section is a section of the Division of Water Resources of the North Carolina Department of Environment and Natural Resources. The Water Sciences Section Chemistry Laboratory is comprised of managers, chemists, technicians, and support personnel. The main laboratory (referred to as the *Central Laboratory*) is located in Raleigh, NC. One satellite laboratory is strategically located in western (Swannanoa, NC) region of the state to provide assistance with time-sensitive tests. The lab is referred to as the *Asheville Regional Office (ARO) Laboratory*.

The Central Laboratory is divided into two analytical programs: the Organic Chemistry Branch and the Microbiology & Inorganic Chemistry Branch. The Organic Chemistry Branch is subdivided into two analytical units: Volatile Organics and Pesticides/Semi-volatile/Sample Preparation. The Microbiology & Inorganic Chemistry Branch is subdivided into three units and a regional laboratory: Chemistry Unit, Microbiology and Metals Unit, Support Unit and the ARO Regional Lab. The Chemistry Unit is further subdivided into two analytical units: Wet Chemistry and Nutrients. The Microbiology and Metals unit is further subdivided into Microbiology and Metals. The Certification Branch is responsible for certifying commercial, industrial, municipal and field laboratories engaged in wastewater analyses and monitoring for North Carolina facilities.

The Water Sciences Section (WSS) is headed by the Section Chief, who is responsible for both the technical and administrative direction of the Section and is committed to the Quality Assurance program described in this manual. The Section Chief is supported by the Environmental Program Supervisors. The Quality Assurance/Quality Control (QA/QC) Coordinator (also referred to as QA Officer) has the responsibility of establishing, implementing and coordinating all activities related to the quality assurance program. The QA/QC Coordinator works independently from groups generating, compiling, and evaluating environmental data and reports directly to the Certification Branch Environmental Program Supervisor III. The QA/QC Coordinator manages the QA/QC program for the two laboratories, including working with lab management and staff to identify improvements to QA systems, and establishing policy for the Water Sciences Section's QA program. The QA/QC Coordinator documents these objectives in the Quality Assurance Manual (QAM) which includes procedures for sample handling, method validation, statistical analyses, and data verification. Quality assurance procedures for other branches of WSS are available online.

An organization chart of the Water Sciences Section is provided in Figure 4.1.

4.1 Responsibilities of Key Positions Pertinent to this QAM

4.1.1 Section Chief - Environmental Program Supervisor IV

Responsible for both the technical and administrative direction of the Water Sciences Section. Responsible for the direction of the activities of the Water Sciences Section which includes various water programs, the WSS Certification Program and the WSS Laboratory. Responsibilities to the WSS Laboratory include providing direction to the various laboratory branches and units regarding actions related to, but not limited to, direction in daily laboratory operations, laboratory accounting and procurement, QA/QC, and customer service. Section Chief’s general duties involve budgeting, making decisions on equipment, the development of policies as needed, mediating personnel issues and signatory authority for all Laboratory Certification actions. Water Sciences Section Chief works with clients on various matters. Any significant changes to the Quality Assurance Manual must be authorized, in writing by the Section Chief.

4.1.2 Certification Branch Supervisor - Environmental Program Supervisor III

Directs Water Sciences Section certification program of certified laboratories; both in-state and out-of-state, which perform environmental analyses. Directs staff, provides administrative program management and future planning for program development. Oversees the Central and Regional Lab Quality Assurance Program. Serves as the section’s liaison to commercial labs, private labs and other programs supported by the WSS Lab. Oversees invoicing and collection of laboratory certification fees, staff training, scheduling, recruitment, hiring, and personnel actions. Assists the Section Chief with budget planning. Establishes work plan documents describing responsibilities, communicates expectations for performance and identifies tracking sources and frequencies. Monitors performance progress toward performance expectations. Designs positions and prepares job descriptions. Reviews and approves audit reports, tracks inspections, and consults with external and internal customers on analytical issues, determines and develops future policies and rules as necessary for the strategic benefit of the laboratory certification program, and issues

de-certifications and other enforcement actions as necessary. Serves as EPA's delegated authority for EPA's DMR QA Proficiency Testing program since the certification program has been deemed to be equivalent. Assures adherence and consistency with existing rules. Develops and promulgates modified rules as needed to maintain the certification program. Responsible for the ensuring that audits of N.C. certified laboratories both field and conventional are performed in a timely manner. Plans and provides for program enhancements through reviews of other state environmental laboratory programs.

4.1.3 Quality Assurance/Quality Control Coordinator - Chemist III

Plans, implements and assesses the Water Sciences Section QA program. Manages the laboratory's blind proficiency program. Manages the QA/QC program for the laboratories, including working with lab management and staff to identify improvements to QA systems, and establishing policy for the labs' QA program. The QA/QC Coordinator documents these objectives in a Quality Assurance Manual (QAM) which includes procedures for sample handling, method validation, statistical analyses, and data verification. Copies of the QAM are made available to all personnel and training in its interpretation is provided. Ensures all routinely used procedures that impact data quality are documented in standard operating procedures (SOPs) that are complete and have been reviewed and approved by both management and the staff responsible for implementing those procedures. Coordinates audits/reviews to assure adherence to the QAM and to identify deficiencies in the QA/QC systems. The QA/QC Coordinator subsequently makes appropriate recommendations for correction and improvement of QA/QC activities by means of written reports. Ensures adequate follow-through actions are implemented in response to audit/review findings. Coordinates external audits and serves as the primary liaison with regulatory agencies to ensure the laboratories' compliance with all pertinent regulatory and accreditation requirements.

4.1.4 Organic Chemistry Branch Supervisor - Environmental Program Supervisor III

Supervises and oversees the daily operation of the Volatile Organics, Pesticides/Semi-volatiles/Extractions Organics units of the Central Laboratory. Responsible for training of staff, developing daily work plan for routine analytical work to ensure that sample holding time requirements and turnaround commitments are met; resolving analytical and instrumental problems; maintaining protocols to meet QA/QC objectives of the laboratory; offering customer support and consulting; supervising chemists and chemistry technicians in their duties; ensuring subordinates are following proper laboratory safety and waste management procedures; and implementing new or modified analytical procedures and instruments. Responsible for technical conduct, evaluation and reporting of all analytical tasks associated with results generated on water, soil, tissue and waste samples submitted for organic analyses. Ensures that only approved procedures are documented and followed, that all data are recorded and verified, and that all deviations from approved procedures are documented. Ensures compliance with quality control objectives and laboratory quality assurance in the organic subsection. Assists Unit Lead Chemists in correcting problems revealed by QA audits and in bringing out-of-control methods back to within established protocol. Certifies analytical reports for release to clients. Performs work performance reviews of the unit chemists and technicians.

4.1.5 Microbiological and Inorganic Chemistry Branch Supervisor - Environmental Program Supervisor III

Supervises the Bio/Chemistry, Metals, and Support units of the Central Laboratory and the Regional Lab. Responsible for technical conduct, evaluation and reporting of all analytical tasks associated with results generated on water, soil, tissue and waste samples submitted for inorganic analyses including trace metal content, minerals, nutrients, and microbiological determinations. Ensures that approved procedures are documented and followed and that all data are recorded and verified, and that all deviations from approved procedures are documented. Ensures compliance with quality control objectives and laboratory quality assurance in the Microbiology and Inorganic Chemistry Branch. Assists Unit Supervisors in correcting problems revealed by QA audits and in bringing out-of-control methods back to within established protocol. Ensures that samples are properly received and documented into both Laserfiche a document management system, and Labworks™ LIMs Data System. Manages the WSS Laboratory Laserfiche system and assists with the WSS Laboratory LIMS system Labworks™. Certifies analytical reports for release to clients. Performs work performance reviews of the unit supervisors.

4.1.6 Chemistry Unit Supervisor - Environmental Program Supervisor II

Oversees the daily operation of the Wet Chemistry and Nutrients units of the Chemistry Unit. Responsible for training of staff, monitoring daily work plan for routine analytical work to ensure that sample holding time requirements and turnaround commitments are met; resolving analytical and instrumental problems; maintaining protocols to meet QA/QC objectives of the laboratory; offering customer support and consulting; supervising chemists and chemistry technicians in their duties; ensuring subordinates are following proper laboratory safety and waste management procedures; and implementing new or modified analytical procedures and instruments. Validates all analytical reports. Performs work performance reviews.

4.1.7 Microbiology and Metals Unit Supervisor - Environmental Program Supervisor II

Oversees the daily operation of the Metals Unit and Microbiology Unit. Responsible for results generated for metals analyses of water, soil, tissue and waste samples submitted to the laboratory. Ensures compliance with quality control objectives and laboratory quality assurance in the Metals Unit. Responsible for training of staff, developing daily work plan for routine analytical work to ensure that sample holding time requirements and turnaround commitments are met; resolving analytical and instrumental problems; maintaining protocols to meet QA/QC objectives of the laboratory; offering customer support and consulting; supervising chemists and chemistry technicians in their duties; ensuring subordinates are following proper laboratory safety and waste management procedures; and implementing new or modified analytical procedures and instruments. Validates all analytical reports. Performs work performance reviews.

4.1.8 Chemists/Chemistry Technicians

These positions involve sample preparation and routine microbiological, chemical and physical analyses of environmental samples including maintenance and troubleshooting of assigned instrumentation. They must adhere to the daily schedule provided by the Supervisor for sample priorities and utilize SOPs for assigned tasks. Perform a variety of routine analyses or preparation procedures to determine and evaluate chemical and physical properties of laboratory samples. Verify proper preservation of samples. Carry out detailed preparation and analysis steps according to published analytical methods and standard operating procedures. Report and review data, and handles routine maintenance of instrumentation. Work under direct supervision of the Unit Supervisor or Environmental Program Supervisor and performs any additional tasks that are assigned. Comply with all policies established in the QA manual and Chemical Hygiene Plan. Perform routine analytical techniques and sample preparation procedures with well-defined standards and SOPs, such as organic extractions, metals digestion, or wet chemistry. Chemists/Chemistry Technicians may have a role in customer support and consultation.

4.1.10 Support Unit Staff

Serve as contact persons to clients at point of sample receipt. Enters sample information into the computerized Labworks™ and Laserfiche systems. Conduct sample receiving procedures including unloading coolers, organizing samples, comparing samples to chain-of-custody documentation, taking sample temperatures, and labeling and archiving samples. Perform routine tasks such as shipping, bottle preparation, acting as liaison with the state and private courier services, and performing sample disposal. The Support Unit Staff References materials regarding hold times, containers, and preservatives. Prepare receipt non-conformance reports and manage sample distribution. Report to the Section Chief. Perform additional tasks as requested such as glassware cleaning. Comply with all policies in the QA manual and Chemical Hygiene Plan.

4.1.11 Administrative Assistant (AAII)

Serves as the requisitioner and receiver on the North Carolina Accounting System (NCAS) for purchasing analytical supplies and instrumentation needed to support seven analytical units and one regional laboratory. Responsible for building maintenance which includes heating and air units, extraction hoods, preventive maintenance, monitoring and maintaining walk in coolers and incubators. Responsible for contact with Facility Management. Manages Water Sciences Section Chemistry Laboratory and regional office fixed assets.

4.1.12 Processing Assistant (PAV)

Checks data entry and reviews final reports for completeness. Receives guest into building assuring that guests sign in when entering and out when leaving the building. Directs phone calls and assists Support Unit when necessary.

4.2 Personnel Training

All activities performed by the Water Sciences Section will be accomplished by qualified personnel. Each individual engaged in the conduct of, or responsible for the supervision of, sample handling and analysis will have education, training, and experience, or a combination thereof, to enable that individual to perform the assigned functions. Each operating unit will have job descriptions for all positions. These job descriptions will specify the minimum qualifications for education, experience, knowledge and skills that are necessary to perform at a satisfactory level. All staff will be encouraged to perform at a level which exceeds expectation. .

4.2.1 Orientation

Each new permanent employee receives a three part orientation including 1) a human resources orientation, 2) a safety orientation and 3) a supervisory orientation. Temporary employees receive all but the human resources orientation.

4.2.1.1 Human Resources Orientation

The human resources orientation provides information on departmental policies, procedures and benefits. New employees also participate in a 6-hour course entitled *Introduction to Organizational Excellence* or equivalent training. This program provides information about the Agency's mission, vision and values; organizational structure; DENR's Quality Program; the expectations of public service, and provides an opportunity for employees to learn how their work contributes to the Agency's mission.

4.2.1.2 Safety Orientation

Safety comes first for DWR WSS Laboratory. The Laboratory has a safety committee composed of an employee from each unit and a Laboratory Safety Officer. The Safety Committee meets once a month or more if needed to discuss safety issues or concerns. The Laboratory Safety Officer along with another Safety Committee member conducts a laboratory safety inspection at least once a year.

Each new employee will take part in a two-tiered safety orientation process that will include a Laboratory safety orientation with the Water Sciences Section Chemistry Laboratory Safety Officer (or safety committee member) and a Laboratory Unit orientation with the employee's Supervisor or unit lead chemist.

The WSS Laboratory safety orientation will include providing the new employee with a copy of the Laboratory Chemical Hygiene Plan (CHP) for the employee to read prior to further training. There will be a follow-up orientation to items covered in the CHP including general safety guidelines for the laboratory (emergency evacuations, eyewashes, personal protective equipment, etc.). In addition, the employee will be provided with an overview of OSHA's Hazard Communication Standard (29 CFR 1910.1200) and the Occupational Exposure to Hazardous Chemicals in Laboratories Standard (29 CFR 1910.1450). This safety orientation is documented on the *New Employee Safety Orientation and Training* form (Figure 4.3) and placed in the employee's Training Documentation File and the Department Training files.

The Water Sciences Section Chemistry Laboratory Unit safety orientation provides additional training specific to the new employee’s job duties and chemical analyses. This training is normally conducted by the unit supervisor or unit lead chemist, and includes information on chemical hazards involved with the unit’s duties and location of Safety Data Sheets (SDS). The employee is required to sign a statement (see *Certification of Unit Training* form in Figure 4.2) indicating that laboratory unit orientation information was made available and that they understand the information. The Unit

Supervisor will allow adequate time, before beginning work, for the new employee to read the unit's standard operating procedures (SOP's) and any other pertinent safety documents, and clarify any areas that are not understood.

The safety orientations will, at a minimum, include:

- Use of chemicals and equipment in the laboratory, the hazards associated with those chemicals and equipment, and appropriate chemical waste disposal procedures.
- Accident/Incident prevention and reporting procedures.
- Laboratory fire safety and evacuation plans.
- A tour of the Laboratory facility.
- Use of Personal Protective Equipment (PPE).

4.2.1.3 Supervisory Orientation

During the supervisory orientation, the new employee's Supervisor provides the employee with a basic understanding of the role of the laboratory within the Division of Water Resources and the basic elements of that individual's position within the laboratory.

Orientations for new employees should be scheduled within the first two weeks of employment, where possible, to allow new employees time to select their benefits and become acquainted with administrative and safety polices prior to beginning analytical duties.

4.2.2 Training

4.2.2.1 Safety and Chemical Hygiene Training

Employees will be apprised of the hazards present in the workplace upon initial assignment to the analytical unit or whenever new chemicals or processes are introduced into the work area. Environmental Program Supervisors, Supervisors, Lead Chemists or Unit Safety Committee member will be responsible for unit-specific chemical hygiene training for new employees. Unit safety training is documented on a *Certification of Unit Training* form (Figure 4.2). A copy is kept in the employee's Training Documentation File and a copy forwarded to the DENR Safety Officer for inclusion in the Department Training files.

At a minimum, employees are to be trained in the following areas:

- The contents of the laboratory Chemical Hygiene Plan (CHP) and how it applies to the analytical unit to which the employee is assigned.
- The location and general contents of the unit Safety Data Sheet (SDS) file. This training can be handled on a hazard class basis for normal chemicals; however, particularly hazardous chemicals must be covered in detail to ensure employees are aware of the chemical's hazardous properties.
- The current Permissible Exposure Limits (PELs) for exposure to chemicals in the analytical unit.
- The detection of leaks or releases of chemicals in the unit and specific cleanup procedures to be used.
- The personal protective equipment (PPE) required to be used in the analytical unit.
- Proper disposal protocol for chemical and sample waste.

Additional safety training courses will be made available from time to time. These courses may be mandatory or optional, depending on the topic. Employees are required to attend all mandatory training and are encouraged to take part in any optional training.

Optional training may include such training as First Aid or CPR training. Mandatory and optional training will also be documented and filed in the employee's Training Documentation File or in the

online NC Learning Center, which is accessed through BEACON, the North Carolina state employee human resources and payroll portal.

Any time substantial changes are made to the CHP, all Water Sciences Section employees will receive an updated plan or training in the changes made to the plan and the process will be documented.

4.2.2.2 Analytical Training

The analytical training of a new employee concentrates on his/her scientific background and work experience to provide the employee with a level of competence so that the individual will be able to function within the defined responsibilities of his/her position as soon as possible. Training is a process used to assist laboratory personnel in their professional development. Training is usually conducted "on-the-job", teaming a qualified analyst with one in training.

Supervisors shall be responsible for providing documentation of training and proficiency for each employee under their supervision. The employee's Training Documentation File indicates what procedures (SOPs) a chemist/chemistry technician is capable of performing either independently or only with supervision. The file should include, at a minimum, the following:

- Job description
- Code of Ethics Statement form
- Value in Performance (VIP) Work Plan
- Orientation forms
- Certificates of coursework completion
- Training forms and associated Initial Demonstration of Capability and Method Detection Limit Studies (IDOCs and MDLs)
- Proficiency testing results
- Audit reports and corrective action responses
- ~~Emergency contact information~~

Each Supervisor is responsible for keeping a Training Documentation file for staff under his or her supervision that is up-to-date and current. If a supervisor relinquishes their duties as supervisor, the Training Documentation Files shall be passed to the new supervisor.

New laboratory personnel are trained in basic lab techniques, safety and chemical hygiene, chemistry theory of the test procedures employed, quality control procedures, the LABWORKS™ LIMS system, record keeping and the operating principles and regulations governing the methods employed by the Water Sciences Section. A designated chemist/technician or the appropriate supervisor closely monitors every new employee until they exhibit proficiency in accepted laboratory techniques. This process includes reading specific SOPs and other associated references. Once a chemist/ technician demonstrates a technological aptitude within the framework of the Quality Assurance program, they will perform an Initial Demonstration of Capability (IDOC) study and a Method Detection Limit (MDL) study (if applicable).

This training process is documented (see SOP/Method Training Summary form - Figure 4.4, IDOC template - Figure 4.5, and MDL template - Figure 4.6) for each chemist and each method and is retained in the employee's Training Documentation File. Upon completion of analytical or QA/QC training, the supervisor will certify that the person is qualified to independently perform the procedures.

Additional training techniques utilized may include:

- Lectures
- Programmed learning
- Conferences and seminars
- Short courses
- Specialized training by instrument manufacturers

- Participation in check-sample or proficiency sample programs

All laboratory personnel are required to review and update all Standard Operating Procedures(SOPs) any time changes are made to procedure that pertain to the work they perform within the laboratory. Personnel will refer to the Guidance for Preparing Standard Operation Procedures located on the DENR intranet portal (http://portal.nc.org/group/wq/chemlabsops) when preparing or updating SOPs. To insure SOPs are accurate, up-to-date and approved in a timely manner, a WSS Laboratory SOP Committee was formed to review both initial and revised SOPs. The Committee consists of members from the analytical units, and all Branch Supervisors and lead by the QA/QC Coordinator. In the WSS laboratories, SOPs are generally written by the Technician, Chemist or Lead Chemist involved in carrying-out the procedure. The Unit Supervisor is responsible for the first tier of review, followed by the each supervisor and finally the Quality Assurance/Quality Control (QA/QC) Coordinator or SOP Review Committee for final signature. The QA/QC Coordinator will serve as SOP custodian and will keep a controlled list of the all current SOPs and revisions. The latest official signed SOPs will be placed onto the DENR Intranet Portal website at (http://portal.ncdenr.org/group/wq/chemlabsops) and are accessible to all analysts and technicians throughout the Water Sciences Section. These versions are either in .pdf format or are write-protected so changes cannot be made without going through the proper approval process. It is the responsibility of the Environmental Program Supervisor to ensure that documentation demonstrating that their employees have read, understand and are using the latest version (including drafts) of SOPs is current and on file.

As an initial and continuing demonstration of proficiency, laboratory analysts are required to successfully analyze annually (at least once per calendar year) either 1) a blind sample, 2) a blind PT sample, 3) at least four consecutive laboratory quality control samples, 4) an authentic sample that has been analyzed by another trained analyst or 5) another acceptable demonstration of capability (e.g., round robins, side-by-side analysis schemes, etc.). Results of initial and continuing proficiency are maintained by laboratory supervisors.

Employees are encouraged to participate in advanced training courses, seminars, and professional organizations and meetings as opportunities and funding become available. Additionally, meetings may be held to discuss procedures, work schedules and problems requiring immediate attention.

At the discretion of the analyst's supervisor, an analyst may demonstrate proficiency in a test method without going through the formal training process. A Statement of Capability form (Figure 4.7) may be used to document the process of “grandfathering" analysts currently performing a procedure or method of analysis. This decision will be based on the analyst's experience, ongoing training workshops, acceptable PT results, or an IDOC study. The completed form will be maintained in the analyst's Training Documentation File.

Review of individual training, IDOC and MDL records are reviewed as they occur and record books are reviewed annually by QA to ensure completeness.

4.3 Facilities

The Central Laboratory building (4405 Reedy Creek Road) was completed and occupied in 1991. The single-story facility includes a full service analytical laboratory operation with all supporting equipment and space. The total facility consists of approximately 18,000 square feet. This includes 3 organic laboratories, 4 inorganic laboratories, a shipping/receiving area, storage areas and office space for staff. Operation and maintenance of the facility is the responsibility of the Division of Facility Management of the Department of Administration. The facility is equipped with centralized water purification and HVAC systems. A floor plan of the Central Laboratory is presented in Figure 4.8.

The Asheville Region Laboratory is housed in the Asheville Regional Office. The total laboratory area consists of approximately 1007 square feet with approximately 61 linear feet of bench space. This includes a main laboratory, a bacteria lab, a small storage area and office space. A floor plan of the ARO Laboratory is presented in Figure 4.9.

Some members of the Laboratory Certification Unit are housed in a Modular building located outside the main Central laboratory building. The total facility consists of approximately 1200 square feet. This includes two main offices, copier room, conference room, six cubicles for staff, storage area and two rest rooms. Operation and maintenance of the facility is the responsibility of the Division of Facility Management of the Department of Administration. The facility is equipped with HVAC system. A floor plan of the Certification Modular is presented in Figure 4.10. All other members are in the Central Laboratory building.

4.3.1 Environment

Laboratory accommodations, test areas, energy sources, lighting, heating and ventilation must be adequate to facilitate proper performance of tests. The environment in which these activities are undertaken shall not invalidate the results or adversely affect the required accuracy of measurement. The laboratory shall provide for the effective monitoring, control and recording of environmental conditions as appropriate. Such environmental conditions may include biological sterility, humidity, and temperature. In instances where monitoring or control of any of the above-mentioned items is specified in a test method or by regulation, the laboratory shall meet and document adherence to those laboratory facility requirements.

4.3.2 Work Areas

There shall be effective separation between neighboring areas when the activities therein are incompatible (e.g., volatile organic chemicals handling and analytical areas). Access to and use of all areas affecting the quality of these activities shall be defined and controlled. Adequate measures will be taken to ensure good housekeeping in the laboratory and to ensure that any contamination does not adversely affect data quality or staff safety.

4.3.3 Building Security

Persons not in the employ of the Water Sciences Section are considered to be visitors to each site. Each visitor to the laboratory must sign in and out in a visitor's logbook and must be escorted by staff while in the laboratory. The buildings are always locked and keys are distributed to all permanent employees. At the Central Laboratory, the main entrance and the Receiving Room (G-098) doors are equipped with an electric lock that can be released by lab personnel. The entrance opposite the main entrance is equipped with a coded lock as well as key lock. Codes are only shared with Water Sciences Section staff. At the Asheville Regional Office Laboratory, the main entrance has a holding area between the front office and the lab area. An Administrative staff person must release an electric lock to allow access to staff offices and the laboratory. Under special circumstances, sample storage coolers may be locked as well and assigned custodians will control access to each. The Certification Program Modular is equipped with a coded lock and consists only of office spaces and conference room. No samples are taken to Certification modular building.

The regional laboratory stores Chain-of-Custody samples in secure or locked areas within the laboratory itself.

4.4 Equipment

4.4.1 Inventory

The laboratories are equipped with advanced analytical equipment including gas chromatographs, gas chromatograph/mass spectrometers, atomic absorption spectrometers, inductively coupled plasma-atomic emission spectrometers, ion chromatograph, flow injection analyzers, fluorometer, UV-VIS spectrophotometers and ancillary analytical equipment and software essential to a quality environmental laboratory. The equipment and software used for testing, calibration and sampling shall be capable of achieving the accuracy required and shall comply with specifications relevant to the environmental tests or calibrations concerned. Instrument serial numbers or assigned ID numbers (for individual instruments or analytical systems) are recorded on the appropriate laboratory data.

Before being placed into service, equipment shall be calibrated or checked to establish that it meets the laboratory's specification requirements and complies with the relevant standard specifications. Similar restrictions apply to devices that may not be the actual test instrument, but are necessary to support laboratory operations. These include,

but are not limited to: balances, ovens, refrigerators, freezers, incubators, water baths, temperature measuring devices (including thermometers and thermistors), thermal sample preparation devices and volumetric dispensing devices (e.g., Eppendorf® or automatic dilutor/dispensing devices) if quantitative results are dependent on their accuracy, as in standard preparation and dispensing. Temperature measuring devices may be put into service initially without checking the calibration if they have certificates of traceability to the National Institute of Standards and Technology (NIST) standards and have been visually inspected for intact Mercury (Hg) or liquid column. They must be checked according to schedule thereafter.

4.4.2 Maintenance/Service

Proper maintenance of laboratory instrumentation is a key ingredient to both the longevity of the useful life of the instrument and providing reliable analyses. Maintenance and service requires an alert analytical staff that recognizes the need for equipment maintenance coupled with support services provided either by in-house staff or by vendor technicians.

4.4.2.1 All staff members have the responsibility for insuring that primary maintenance is carried out on instrumentation. The primary elements of the equipment maintenance program include:

- All major equipment receives a daily check for such things as pump operation, instrument settings, indicator readings, mechanical operation, clean tubing, clean cells, etc.
- Routine preventive maintenance on all major equipment is performed as needed and records are kept in maintenance logs for all repairs;
- Instrument utilization records are maintained in the form of analysis logs or instrument run logs;
- A conservative inventory of critical spare parts is maintained for high-use instrumentation;
- Vendor-produced operation and maintenance manuals (where available) are maintained for all laboratory instrumentation.

4.4.2.2 Daily maintenance responsibilities are generally delegated to the chemists/chemistry technicians. This measure improves overall lab productivity by minimizing instrument downtime. Other benefits include job knowledge enhancement, maintenance cost reduction and less frequent out-of-control situations. In a situation where the analyst is unable to rectify a problem with the instrument, supervisor steps in to help prior to calling the manufacturer service representative.

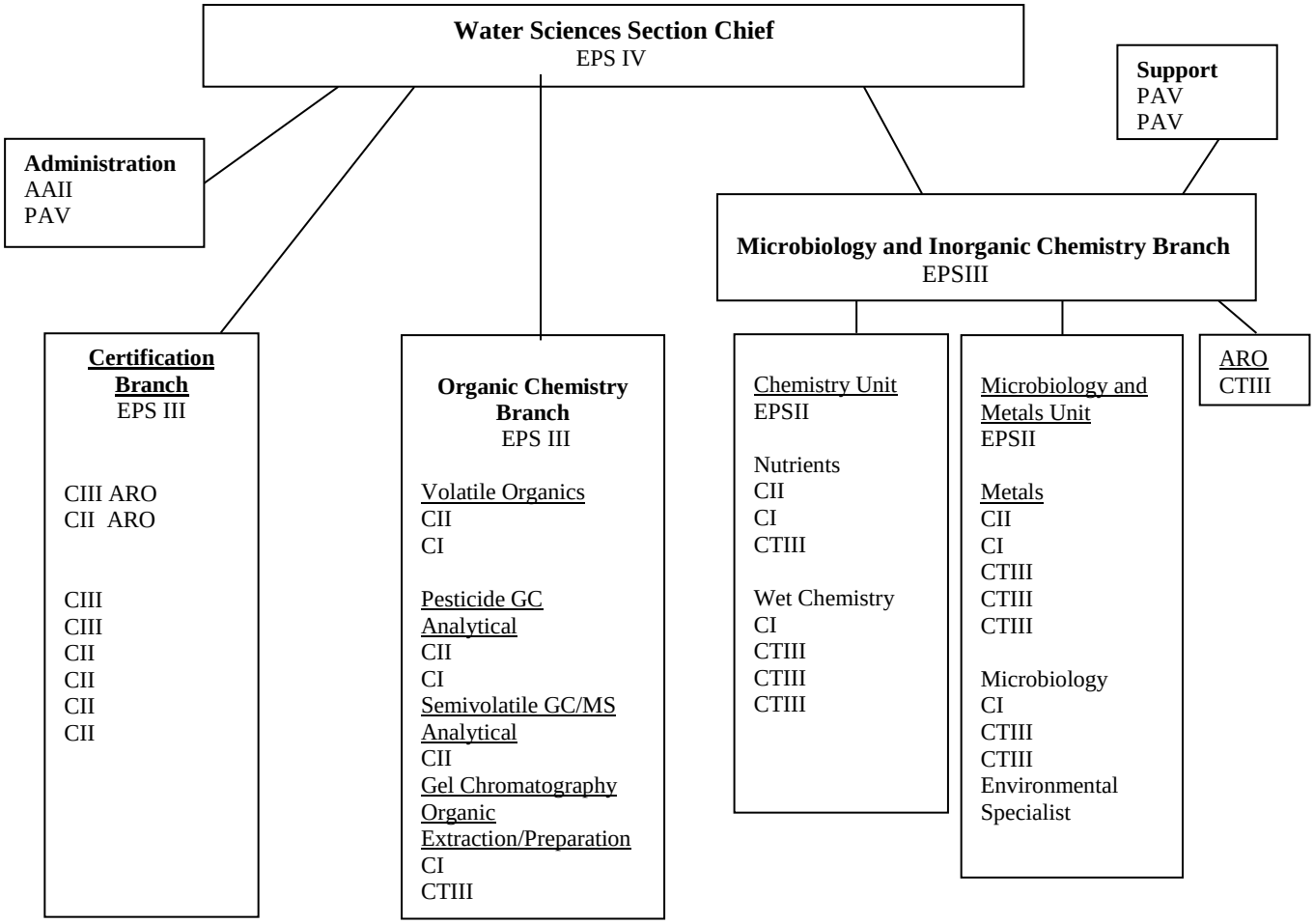
Some of the instruments are under service contract with the manufacturer and in most cases include preventative maintenance checks by their service technicians. Most service contracts are written with 48-72 hour response times to service calls. All maintenance is documented in the maintenance logbooks to be used as a source of information in solving future instrument problems.

Many consumable parts are kept in stock. Examples may include, pump tubing for Flow Injection Analysis (FIA) systems and spare columns for Gas Chromatography (GC) techniques. In many cases, vendors are able to provide for overnight shipment of parts that do not require manufacturer's installation.

4.4.3 Equipment Redundancy

Redundant equipment and instruments are maintained where feasible. This helps in the case whenever one instrument goes down, another instrument can be used (e.g., 2 gas chromatographs or a backup DO meter) to meet hold times or client due dates. In some cases, samples may be routed to the Asheville Regional Office Laboratory if they have the capability and if the samples will meet the published hold times.

Figure 4.1. North Carolina Division of Water Resources Water Sciences Section Organization Chart



C	Chemist
CT	Chemistry Technician
EPS	Environmental Program Supervisor
PA	Processing Assistant
AA	Administrative Assistant

Figure 4.2. Certification of Unit Training Form

Certification of Unit Safety Training - Laboratory

Water Sciences Section - Division of Water Resources

Employee Name:	
Laboratory Unit:	
Supervisor Name:	
Designated Trainer:	

With my signature below, I acknowledge that I have been instructed by my unit supervisor (or designated trainer) on the health and safety hazards present in my current work area(s) (list room numbers:_____) and the proper safety procedures to follow when working in these areas. The hazards and procedures are outlined in the Laboratory Section Chemical Hygiene Plan, as well as Standard Operating Procedures for the lab unit.

I understand these hazards and accept them as a necessary part of my work.

I will follow the proper safety procedures in my work area at all times.

Employee Signature	**Date**
Supervisor Signature	**Date**

M:/LABFORMS/TRF-003-1 (COU) Revised: 5/2014

Figure 4.3. New Employee Safety Orientation and Training Form

New Employee Safety Orientation & Training

Chemistry Laboratory - Water Sciences Section - N.C. Division of Water Resources

Date of Orientation:	
Name of Employee:	
Orientation Instructor:	

Safety Overview	
	Recognizing Work-Area Hazards
	Safety Devices available in Laboratory and Unit
	Reporting Accidents and Injuries
	First Aid Kits
	Fire Prevention Guidelines
	Housekeeping Rules, Clothing, Washing Lab Coats
Personal Protective Equipment	
	Location
	Instructions for Use
	Additional Protective Equipment used in Unit
Evacuation Plan	
	When to Evacuate Building and Where to Go
	Alarm System
General Laboratory Hazards	
	Equipment Hazards
	Electrical Hazards
	Compressed Gas Cylinders
	Autoclaves
	Vacuums
	Noise Exposure
Fume Hoods	
	When and How to Use a Fume Hood
	Alarm
Chemicals	
	Overview of Chemicals used in the Laboratory
	Hazardous Chemicals used in Unit
	Material Safety Date Sheets
	Storage, Compatibility, Spill Response
	Transporting Chemicals
	Disposal of Hazardous and Toxic Chemicals
Other Safety Issues for Unit	

By signing below, the employee and instructor verify that the above items were discussed and understood.

Signature of Employee **Date**

Signature of Instructor **Date**

M:/LABFORMS/TRF-005-1 (NES) Revised: 5/2014

Figure 4.4. SOP/Method Training Summary Form

SOP/METHOD TRAINING SUMMARY

Trainee		**Instrument(s)**	
Date training began		**Date of completion**	
SOP(s) reviewed		**Reference method(s)**	
Method/Parameter		**Unit**	

I. METHOD/PARAMETER

____ Reference Method/SOP
____ Basic Method/Instrument Theory
____ Safety Precautions
____ Waste Handling
____ Regulatory Standards
____ Routine Maintenance
____ Interferences
____ Extraction/Preparation

II. QUALITY CONTROL

____ Calibration Curve, Initial Calibration Verification and Continuing Calibration Verification
____ Precision/Accuracy
____ MDL study
____ Review of COC procedures
____ Documentation(sequences, maintenance logbooks, benchsheets, observations, modifications, standards/reagent prep.)
____ QC Requirements (MS/MSD, QCS, duplicates, blanks, surrogates, internal standard, interference checks, etc.)
____ Miscellaneous QC (retention time window studies, IDL, etc.)
____ Non-Conformance and Corrective Action Documentation (SCUR/SAR)

III. DATA HANDLING AND REPORTING

____ Review Equations and Calculations (concentrations, dry/wet weight)
____ Data Entry (LABWORKS™)
____ Significant Figures
____ Reporting Dilutions
____ Reporting Qualified Data

IV. GENERAL TRAINING

Describe what was discussed. General Training topics might include sample receiving, aseptic technique, shipping, operation of support equipment (e.g., pH meter), training course attendance, etc. Attach additional pages if necessary.

_____

_____

RESULTS OF START-UP QC:

IDOC Results	Acceptable:	Y / N / NA	Attach a copy of the IDOC study summary.
PT Sample Results	Acceptable:	Y / N / NA	Attach a copy of PT sample result summary.
MDL Study	Completed:	Y / N / NA	Attach a copy of the MDL study summary.

SIGNATURE AUTHORIZATION:

By signing, the trainee verifies that he/she has received, read and understands the SOP(s), reference method and any other related materials required to effectively perform the subject analysis or general procedure. Signature of the Supervisor, Branch Manager and QA/QC Coordinator verifies that the analyst has met the minimum requirements of demonstration of capability to perform the subject analysis or procedure. If additional training is required, this form should not be signed.

Trainee:_____Signature:_____ Date:_____
Supervisor:_____Signature:_____Date:_____
BranchManager:_____Signature:_____Date:_____
QA/QCCoordinator:_____Signature:_____Date: _____

Figure 4.5. IDOC Summary Form

Initial Demonstration of Capability (IDOC)
Certification Statement

Laboratory Name:		**Analytical Method:**	
Analyst Name:		**SOP#:**	
Date:		**Instrument/serial #:**	
Sample Prep. Method:		**Column:**	
Sample Prep. SOP#:		**Detector:**	
Matrix:		**Cleanup/Modification:**	

Analyte	Spike conc.	Units	1	2	3	4	Mean Recovery %	Mean Value X	Acceptance Range of X[1]	Standard Deviation s	Acceptance Criteria of s[1]	% RSD[2]	P/F
LRB data													

P = pass F = fail

[1]Cite reference**. _____.**

[2]% RSD = % relative standard deviation = (s/X) 100

Comments:

_____

We, the undersigned, CERTIFY that:
The analysts identified above, using the cited test method(s), which is in use at this facility for the analyses of samples have met the Initial Demonstration of Capability. The test method(s) was performed by the analyst(s) identified on this certification. A copy of the test method(s) and the laboratory-specific SOPs are available for all personnel on-site. The data associated with the demonstration of capability are true, accurate, complete and self-explanatory. All raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well organized and available for review by authorized assessors.

_____ _____ _____
Chemist's/Technician's Name (print) Signature Date

_____ _____ _____
Branch Manager's Name (print) Signature Date

_____ _____ _____
Supervisor's Name (print) Signature Date

_____ _____ _____
Quality Assurance Officer's Name (print) Signature Date

Figure 4.6. MDL Summary Form

Method Detection Limit (MDL) Study

Laboratory Name:		**Analytical Method:**	
Analyst(s) Name(s):		**SOP#:**	
Date:		**Instrument/serial #:**	
Sample Prep. Method:		**Column:**	
SOP#:		**Detector:**	
Matrix:		**Cleanup/Modification:**	

Analyte	Spike conc.	Units	1	2	3	4	5	6	7	Mean Recovery %	Average Recovery X	Standard Deviations	MDL	PQL
LRB data														

MDL = t (n-1, 1-a = 0.99) (s)
t = Student's t values appropriate for 99% confidence level. Table of Student's t values can be found in 40 CFR Part 136, Appendix B.
PQL = 3 to 5 times the calculated MDL.

Comments:
_____

_____ _____ _____
Chemist's/Technician's Name Signature Date

_____ _____ _____
Branch Manager's Name Signature Date

_____ _____ _____
Supervisor's Name Signature Date

_____ _____ _____
Quality Assurance Officer's Name Signature Date

Figure 4.7. Statement of Capability Form

STATEMENT OF CAPABILITY
(used to "grandfather" in current analysts)

_____ has been performing the following analyses:
(analyst's name)

Method / Parameter	SOP #	Start Date	End or Current Date

The analyst is deemed proficient in the performance of the analyses listed above because (check all that apply):

☐ Analyst's experience. Comment:_____
_____
_____

☐ The analyst has demonstrated the use and understanding of the SOP and referenced methods.
☐ Acceptable results on past PT samples. Attach examples.
☐ Acceptable IDOC on four QCS replicates. Attach IDOC study summary.

APPROVED BY:

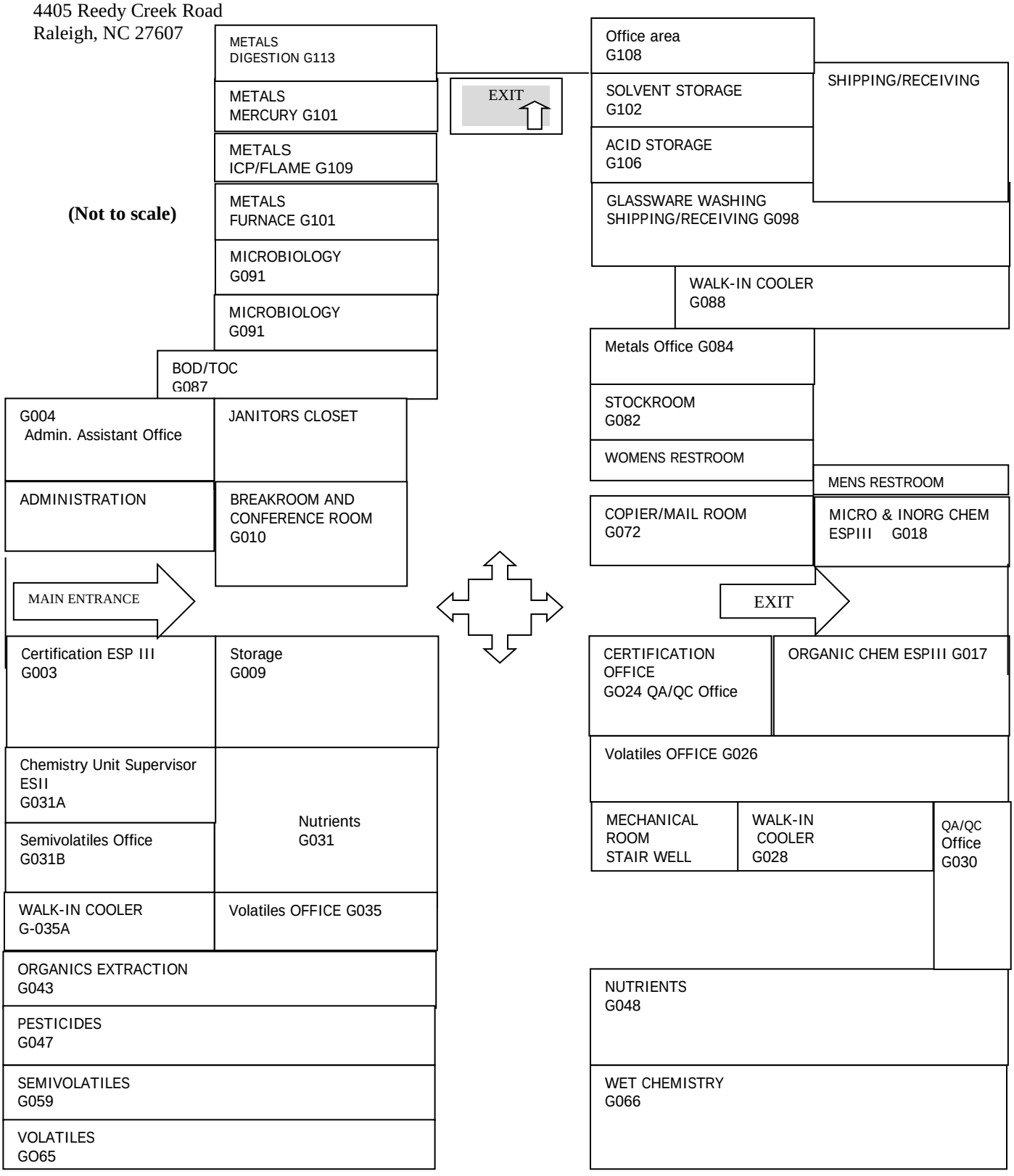
Supervisor: _____ Date: _____

Branch Manager: _____Date: _____

QA/QC Coordinator: _____Date: _____

Figure 4.8. Central Laboratory Floorplan

Central Laboratory
4405 Reedy Creek Road
Raleigh, NC 27607



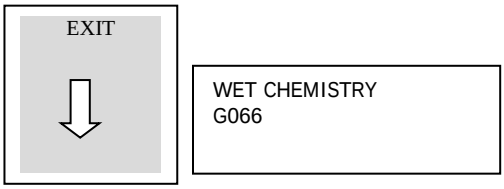
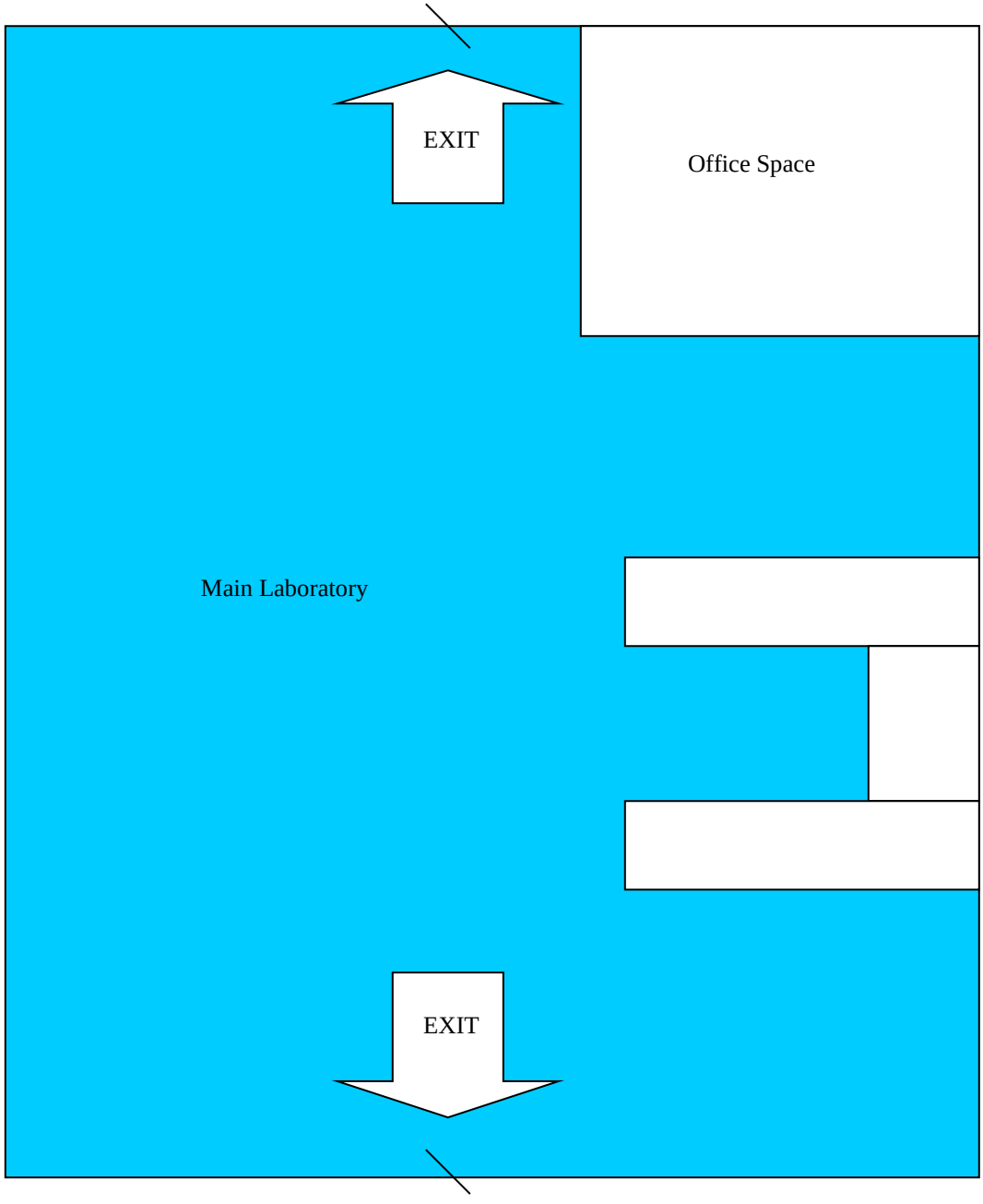

EXIT
WET CHEMISTRY
G066

Figure 4.9. Asheville Regional Laboratory Floor Plan
Asheville Laboratory
2090 US Highway 70
Swannanoa, NC 28778

(not to scale)

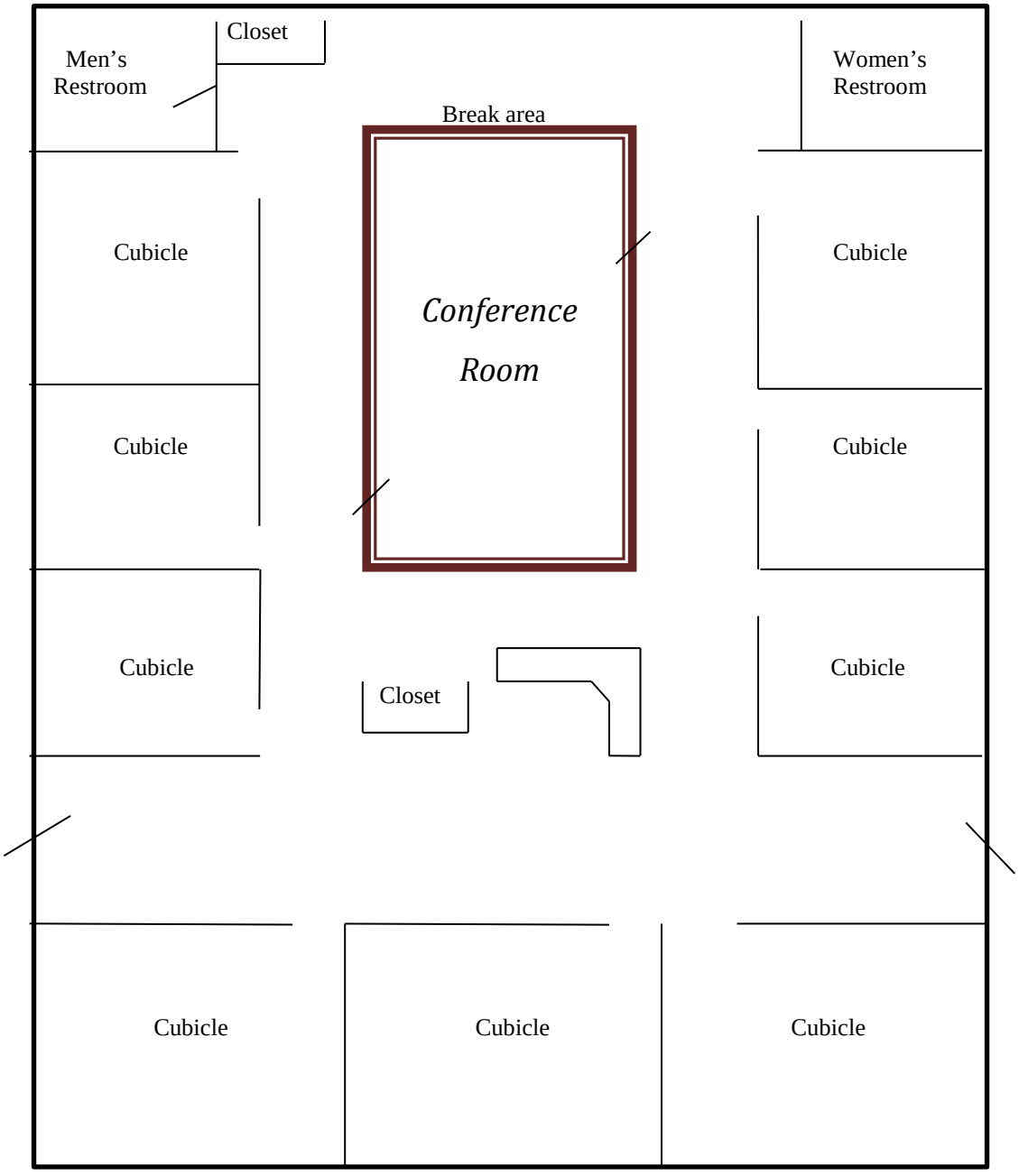


Lab area is shaded

Figure 4.10. Lab Certification Modular Building Floorplan

Laboratory Certification 4405 Reedy Creek Road Raleigh, NC 27607

(not to scale)



5.0 QA Targets for Precision, Accuracy and MDLs/PQLs

The DWR Water Sciences Section quality assurance objectives are described in terms of precision, accuracy, representativeness, and comparability. Criteria for data quality indicators such as matrix spikes, laboratory control samples and duplicate sample precision are specified in this section.

5.1 Quality Assurance Objectives

5.1.1 Precision

The laboratory objective for precision is to meet the precision required by or demonstrated for the analytical methods on similar samples (i.e., limits generated from historical data) and to meet data for the analyses published by the US EPA or state regulatory requirements. Precision is defined as the degree of reproducibility of repetitive measurements under a given set of analytical conditions (exclusive of field sampling variability). It is the degree of mutual agreement among independent measurements as the result of repeated application of the same process under similar conditions. Precision is documented on the basis of replicate analysis, usually duplicate or matrix spike duplicate samples. Limits are based on historical data or in some cases default limits until enough data points are generated to calculate statistically valid in house limits. Limits are in some cases dictated by method.

5.1.2 Accuracy

The laboratory objective for accuracy is to meet the performance for accuracy required by or demonstrated for the analytical methods on similar samples (i.e., limits generated from historical data) and to meet the recovery data published by the US EPA or state regulatory requirements. Accuracy is defined as the degree agreement of a measured value with the true or expected value of the quantity of concern (per John K. Taylor, in *Quality Assurance of Chemistry Measurements*). It is a statistical measurement of correctness and includes components of random error (variability due to imprecision) and systematic error. It reflects the error associated with a measurement. A measurement is accurate when the value reported does not differ from the true value or known concentration of the spike or standard. Analytical accuracy is typically measured by determining the percent recovery of known target analytes that are spiked into a field sample (i.e., a surrogate or matrix spike) or reagent water (i.e., laboratory control sample or QC check sample). Surrogate compound recovery is reported and is used to assess method performance for each sample analyzed for volatile and semivolatile organic compounds. A statement of accuracy is expressed as an interval of acceptance recovery about the mean recovery. Limits are based on historical data or in some cases default limits until enough data points are generated to calculate statistically valid in house limits. Limits are in some cases dictated by method. Limits are in some cases also generated from historical data as compared to EPA CLP SOW guidelines.

5.1.3 Representativeness

The laboratory objective for representativeness is to provide data which is representative of the sampled medium. Representativeness is defined as the degree to which data represent a characteristic of a population or set of samples and is measurement of both analytical and field sampling precision. The representativeness of the analytical data is a function of the procedures used in procuring and processing the samples and subsequent sub samples. The representativeness can be documented by the relative percent difference between separately procured, but otherwise identical samples or sample aliquots.

5.1.4 Comparability

The comparability objective is to provide analytical data for which the accuracy, precision, representativeness and reporting limits statistics are similar to these quality indicators generated by other laboratories for similar samples, and data generated by the Water Sciences Section Chemistry Laboratory over time.

The comparability objective is documented by inter-laboratory studies carried out by regulatory agencies or carried out for specific projects, by comparison of periodically generated statements of accuracy, precision and reporting limits with those of other laboratories and by the degree to which approval from the US EPA or other pertinent regulatory agencies is obtained for any procedure for which significant modifications have been made.

5.2 QA Targets

Examples of analytes, preparative and analytical methods, matrices, accuracy and precision targets, MDLs and PQLs for analyses performed by the Water Sciences Section Chemistry Laboratories are presented in Tables 5.1 through 5.10. Unless otherwise noted, the limits in these tables are examples of laboratory generated limits. Some acceptability limits are derived from US EPA methods when they are provided. Where US EPA limits are not provided, the Water Sciences Section Chemistry Laboratories have adopted interim limits or developed limits from general laboratory practice or evaluation of data from similar matrices. Acceptability of QC will be determined as compared to these tables. Data may be accepted where QC falls outside these limits if probable cause can be attributed to the matrix and laboratory control samples show that the method is in control. Deviations are to be fully documented in the final report. In instances where a LCS limit is not available, a limit of 70-130% recovery is acceptable until in-house limits can be generated. In some cases, wider default limits may be set with the QA/QC Officer and ESPIII approval. In the absence of in-house or method-defined limits, the following guidelines may be used to determine interim limits for matrix spike and matrix spike/matrix spike duplicates:

MS	60-140%
MS/MSD	20% RPD

Some criteria may need to be wider based on prior knowledge of the compound (e.g., phenols in EPA 8270D).

5.3 Statistically Derived Limits

Statistically derived precision and accuracy limits are required by selected methods and programs. The Water Sciences Section will routinely utilize statistically derived and the lowest calibration standard concentration must be equivalent to the PQL, (based upon laboratory derived data) to evaluate method performance and determine when corrective action may be appropriate. These limits must be equal to or more restrictive than the limits specified in the referenced method. The laboratory may periodically update the limits. The analysts are instructed to use the current limits posted in the laboratory (dated and approved by the Quality Assurance Officer) and entered into a master log. The Quality Assurance Officer or each analytical unit maintains an archive of the limits used within the laboratory.

Where EPA acceptability criteria does not exist for a given method being utilized for the first time, the laboratories will establish control limits derived from a minimum of four data points. Until verified by a statistically significant data population, a reasonable interim value will be assigned and the control limits will be considered as advisory limits only and will not automatically initiate a corrective action if they are not met.

Where in-house limits are generated, limits cannot be less stringent than method defined limits. Most stringent QC is adopted where methods are combined for analyses. Exceptions will be noted in the parameter analysis SOP.

5.4 Method Detection Limits

Method Detection Limits (MDLs) are set such that the constituent concentration, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank. MDLs are determined using the method specified in the Federal Register, 40 CFR Part 136 Appendix B. MDLs are based on the latest MDL study available at the time this document was published and may be superseded by the results from new studies. MDLs are updated annually for some parameters (depending on method requirement), every other year for others **or** any time there is a significant change in laboratory operations, or instrument performance. Analysis may be spread out over a period of time or analyzed at one time.

MDL study is not required for the following analyses: BOD-CBOD, COD, TOC, Coliform (Total and fecal), Specific Conductivity, pH, Color and Solids,

5.5 Practical Quantitation Limits

The Practical Quantitation Limit (PQL) is defined as the lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. PQLs are subjectively set at some multiple of typical MDLs for reagent water (generally 3 to 10 times the MDL depending upon the parameter or analyte and based on the analyst's best professional judgement, the quality and age of the instrument and the nature of the samples) rather than explicitly determined. PQLs may be nominally chosen within these guidelines to simplify data reporting and, where applicable, are generally equal to the concentration of the lowest non-zero standard in the calibration curve. PQLs are adjusted for sample size, dilution and % moisture. For parameters that are not amenable to MDL studies, the PQL may be defined by the sample volume and buret graduations for titrations or by minimum measurement values set by the method for method-defined parameters (e.g., BOD requires a minimum DO depletion of 2.0 mg/L, fecal coliform requires a minimum plate count of 20 cfu, total suspended residue requires a minimum weight gain of 2.5 mg, etc.). Additionally, some EPA methods prescribe Minimum Levels (MLs) and the lab may set the PQL equal to this method-stated ML. Determination of PQL is fully described in the laboratory's analytical Standard Operating Procedure (SOP) document.

Published PQLs may be set higher than experimentally determined PQLs3) at a concentration elevated to a level greater than 3 to 5 times the calculated MDL.to:

1) avoid observed positive interferences from matrix effects or common reagent contaminants, or
2) for reporting convenience (i.e., to group common compounds with similar but slightly different experimentally determined PQLs)

Values between the MDL and PQL are currently not reported; however, can be reported as required by a client; these values, when reported, are always reported with a qualifier code (N3). Additionally, non-detected analytes are always reported as less than the PQL.

Note: Qualifier Codes and their definitions are found in Appendix II.

5.6 QA Target Tables

The QA targets' table list EXAMPLEs of each parameter's QC acceptance criteria. Updated PQL limits are available at:

Tables 5.1 thru 5.10 are ONLY EXAMPLEs of the online tables and should not be used for verification of accuracy.

Note that MDLs and PQLs for soil/sediment matrices are based on method-specific sample dry weights. Detection limits may vary from that published, due to moisture content, dilution effects, interferences, special reporting requirements, etc.

The QA targets for most inorganic analyses are within the range of 90 - 110 % for accuracy for aqueous samples, unless other limits are stated in the method. For inorganic matrix spiked duplicates (MSD) the acceptable precision limit is <20% RPD, unless laboratory-generated data indicate that tighter control limits can be met. Exceptions would be for solid samples due to complex matrices and low level standards at the PQL is (75%-125%), unless other limits are stated in the method or historical data indicates these limits cannot be met based on calculated control limits. The organic QA target are statutory in nature; warning and control limits for organic analyses are initially set for groups of compounds based on preliminary method validation data or in some cases default limits until enough data points are generated to calculate statistically valid in house limits. When additional data is available, the QA targets may be reconsidered. QA targets are routinely re-evaluated at least annually and generally semi-annually and updated if necessary against laboratory generated data. In some cases they may be compared to EPA CLP SOW to insure targets continue to reflect realistic methodologically achievable goals.

Each table in this section is formatted in the same way and the following conventions apply to all of them:

- Matrices are denoted as follows:
  W: surface, ground and waste water
  S: soil, sediment, solid
  T: tissue
- Acronyms used in the method citations are:
- **EPA** refers to methods published in *Methods for Chemical Analysis of Water and Wastes*, EPA 600/4-79-020, March 1983, 40 CFR Part 136, Appendices A-D and *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, SW-846 (3rd. Edition) as amended by Updates I, II, IIA, III and IV.
- **SM##** refers to methods published in *Standard Methods for the Examination of Water and Wastewater*, APHA. Each citation is followed by year of approval by Standard Methods Committee. For example, **SM5210B – 2001; SM5210 is the method and 2001** refers to the accepted year of approval by the Standard Methods Committee for a method.
- **ASTM** refers to methods published in the *Annual Book of ASTM standards*, Vols. 11.01 and 11.02, 1999 (2012),(2014)
- **HACH** refers to methods published in *Hach Water Analysis Handbook*, 3rd (5th. Edition) Edition, Hach Company Loveland, CO, 1997 (2012).
- **QuikChem** refers to methods published by Lachat Instruments, Milwaukee, WI.
- **USGS** refers to *Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments*, U.S. Department of the Interior, Techniques of Water-Resource Investigation of the U.S. Geological Survey, Denver, CO, Revised 1989.
- Modified methods are designated with an "M" after the method number.

Table 5.1 EXAMPLES of QA Targets for METALS Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method[1]	Matrix	Spike[2] Recovery Range (%)	QCS[3] Accuracy Range (%)	Precision % RPD	MDL	PQL
Aluminum	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994/ 200.8 Rev. 5.4 1994	W	70-130	90-110	≤20	3.10 / 1.67 µg/L	50 µg/L
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[5]	1.0 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Antimony	EPA 200.2M Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994	W	70-130	90-110	≤20	0.014 µg/L	10 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Arsenic	EPA 200.2M Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.9 Rev. 2.2 1994	W	70-130	90-110	≤20	0.327 / 0.405 µg/L	2.0µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Barium	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.132 µg/L	10 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994 / 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.7 Rev. 4.4 1994	T	70-130	90-100	≤20	NA[5]	0.20 mg/kg

Table 5.1 EXAMPLES of QA Targets for METALS Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method[1]	Matrix	Spike[2] Recovery Range (%)	QCS[3] Accuracy Range (%)	Precision % RPD	MDL	PQL
Beryllium	EPA 200.2M Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.015 / 0.098 µg/L	5.0 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.10 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 4.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Boron	EPA 200.2M Rev. 2.8 1994	EPA 200.7 Rev .4.4 1994	W	70-130	90-110	≤20	(See Note 4)	50 ug/L
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[5]	1.0 mg/kg
Calcium	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.014 mg/L	0.10 mg/kg
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[5]	2.0 mg/kg
Cadmium	EPA 200.2M Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.9 Rev. 2.2 1994	W	70-130	90-110	≤20	0.0170 / 0.209µg/L	0.50 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Chromium, Total	EPA 200.2M Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.7 Rev.4.4 1994	W	70-130	90-110	≤20	0.145 / 0.534 µg/L	10 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0. 20 mg/kg

Table 5.1 EXAMPLES of QA Targets for METALS Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method[(1)]	Matrix	Spike[(2)] Recovery Range (%)	QCS[(3)] Accuracy Range (%)	Precision % RPD	MDL	PQL
Cobalt	EPA 200.2M Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.012 / 0.623 µg/L	50 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[(5)]	1.0 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[(5)]	0.10 mg/kg
Copper	EPA 200.2M Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.9 Rev. 2.2 1994	W	70-130	90-110	≤20	0.054 / 0.661 µg/L	2.0 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[(5)]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[(5)]	0.10 mg/kg
Iron	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	6.19 µg/L	50 µg/L
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[(5)]	1.0 mg/kg
Lead	EPA 200.2 Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.9 Rev. 2.2 1994	W	70-130	90-110	≤20	0.013 / 0.737 µg/L	2.0µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[(5)]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[(5)]	0.10 mg/kg
Lithium	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.585 µg/L	25 µg/L
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[(5)]	0 2.5 mg/kg

Table 5.1 EXAMPLES of QA Targets for METALS Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method[(1)]	Matrix	Spike[(2)] Recovery Range (%)	QCS[(3)] Accuracy Range (%)	Precision % RPD	MDL	PQL
Magnesium	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.006 mg/L	0.10 mg/L
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[(5)]	2.0 mg/kg
Manganese	EPA 200.2M Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994/ 200.8 Rev. 5.4 1994	W	70-130	90-110	≤20	0.083 / 0.219 µg/L	10 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[(5)]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[(5)]	0.10 mg/kg
Mercury	EPA 245.1 Rev. 3.0 1994	EPA 245.1 Rev. 3.0 1994	W	70-130	90-110	≤20	0.035 µg/L	0.20 µg/L
	EPA 245.5M Rev. 1.0 2001	EPA 245.5 Rev. 1.0 2001	S	70-130	90-110	≤20	0.004 mg/kg	0.02 mg/kg
	EPA 245.6 Rev. 2.3 1991	EPA 245.6 Rev. 2.3 1991	T	70-130	90-110	≤20	0.006 mg/kg	0.02 mg/kg
Mercury Low level	EPA 1631E 2002	EPA 1631E 2002	W	71-125			0.20 ng/L	1.0 ng/L
Molybdenum	EPA 200.2 Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994	W	70-130			0.0158	10 µg/L
	EPA 200.2 Rev. 2.8 1994	EPA 200.2M Rev. 2.8 1994	T	70-130	90-100	≤20	N/A[(5)]	0.10 mg/kg
Nickel	EPA 200.2 Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.9 Rev. 2.2 1994	W	70-130	90-110	≤20	0.093 / 2.10 µg/L	2.0 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[(5)]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[(5)]	0.10 mg/kg
Potassium	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.003 mg/L	0.10 mg/L
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[(5)]	2.0 mg/kg

Table 5.1 EXAMPLES of QA Targets for METALS Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method[1]	Matrix	Spike[2] Recovery Range (%)	QCS[3] Accuracy Range (%)	Precision % RPD	MDL	PQL
Selenium	EPA 200.2 Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.9 Rev. 2.2 1994	W	70-130	90-110	≤20	0.149 / 1.298 µg/L	5.0 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 4.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Silver	EPA 200.2 Rev. 2.8 1994	EPA 200.8 Rev. 5.4 1994 / 200.9 Rev. 2.2 1994	W	70-130	90-110	≤20	0.0103 / 0.967µg/L	1.0 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Sodium	EPA 200.2M Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994	W	70-130	90-110	≤20	0.014 mg/L	0.10 mg/L
	EPA 3050B	EPA 200.7 Rev. 4.4 1994	S	70-130	90-110	≤20	NA[5]	2.0 mg/kg
Strontium	EPA 200.2 Rev 2.8 1994	EPA 200.8 Rev. 5.4 1994	W	70-130	90-110	≤20	0.029	10
	EPA Method 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Thallium	EPA 200.2 Rev. 2.8 1994	EPA 200.8 Rev. 5.41994	W	70-130	90-110	≤20	0.012 µg/L	2.0 µg/L
	EPA 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg
Tin	EPA 200.2 Rev 2.8 1994	EPA 200.8 Rev. 5.4 1994	W	70-130	90-110	≤20	0.322	10
	EPA Method 3050B	EPA 200.8 Rev. 5.4 1994	S	70-130	90-110	≤20	NA[5]	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA[5]	0.10 mg/kg

Table 5.1 EXAMPLES of QA Targets for METALS Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method(1)	Matrix	Spike(2) Recovery Range (%)	QCS(3) Accuracy Range (%)	Precision % RPD	MDL	PQL
Vanadium	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994 / 200.8 Rev. 5.4 1994	W	70-130	90-110	≤20	0.952 / 1.80 µg/L	25 µg/L
	EPA 3050B	EPA 200.7 Rev.4.4 1994	S	70-130	90-110	≤20	NA(5)	0 0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.8 Rev. 5.4 1994	T	70-130	90-110	≤20	NA(5)	0.10 mg/kg
Zinc	EPA 200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4 1994 / 200.8 Rev. 5.4 1994	W	70-130	90-110	≤20	1.69 / 0.145 µg/L	10 µg/L
	EPA 3050B	EPA 200.7 Rev4.4 1994	S	70-130	90-110	≤20	NA(5)	0.20 mg/kg
	EPA 200.3 Rev. 1.0 1994	EPA 200.7 Rev.4.4 1994	T	70-130	90-110	≤20	NA(5)	0.10 mg/kg
Titanium	200.2 Rev. 2.8 1994	EPA 200.7 Rev. 4.4	W	70-130	90-110	≤20	0.288 µg/L	10 µg/L
	EPA 3050B	EPA 200.7 Rev. 4.4	S	70-130	90-110	≤20	NA(5)	0.20 mg/kg

(1) Where two methods are listed, the first one is preferred for analysis.
(2) References: EPA Method 200.7, Section 9.4.3, Revision 4.4 May 1994. EPA Method 200.8, Section 9.4.3, Revision 5.4 May 1004. EPA Method 200.9, Section 9.4.3, Revision 2.2 May 1994
(3) The QCS (Quality Control Sample) must be from a different source than calibration standards and have a "Certificate of Analysis" document from the vendor. The accuracy range listed is for QCS containing concentrations at the midrange of calibration curve. QCS with concentration at the lower end of the calibration curve will use "Acceptance Limits based on US EPA WS and WP Interlaboratory Study" listed on the Certificate of Analysis sheet or calculated control limits.
(4) MDL for Boron has not been determined as of 01/13/2015. (There were added during coal ash emergencies)
(5) NA = Not Available. MDL values have not been determined for sediment "S" and tissue "T", except for Hg.

Table 5.2 EXAMPLES of QA Targets for NUTRIENTS Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike[1] Accuracy Range (%)	LCS[1] Accuracy Range (%)	Precision % RPD	MDL (mg/L)	PQL (mg/L)
Ammonia Nitrogen as N	N/A	EPA 350.1 Rev. 2.0 1993 QUIK CHEM 10-107-06-1-J	W	90-110	90-110	≤10	0.001	0.02
Total Kjeldahl Nitrogen as N	N/A	EPA 351.2 Rev. 2.0 1993 QUIK CHEM 10-107-06-2-H	W	80-120	90-110	≤20	0.05	0.20
Nitrate + Nitrite Nitrogen as N	N/A	EPA 353.2 Rev. 2.0 1993 QUIK CHEM 10-107-04-1-C	W	90-110	90-110	≤10	0.002	0.02
Phosphorous, Total as P	N/A	EPA 365.1 Rev. 2.0 1993 QUIK CHEM 10-115-01-1-EF	W	90-110	90-110	≤10	0.004	0.02
Phosphorous, Dissolved as P	N/A	EPA 365.1 Rev. 2.0 1993 QUIK CHEM 10-115-01-1-EF	W	90-110	90-110	≤10	0.004	0.02
Orthophosphate as P	N/A	EPA 365.1 Rev. 2.0 1993 QUIK CHEM 10-115-01-1-A	W	90-110	90-110	≤10	0.004	0.02
NO2 as N	N/A	EPA 353.2 Rev. 2.0 1993 QUIK CHEM 10-107-04-1-C	W	90-110	90-110	≤10	0.002	0.01

[1] Quik Chem Lachat Methods

Table 5.3 EXAMPLES of QA Targets for MICROBIOLOGY Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL	PQL
BOD_5	N/A	SM5210 B- 2001	W	N/A	198 ± 30.5[1]	<20	N/A	2.0mg/L
$CBOD_5$	N/A	SM5210 B- 2001	W	N/A	164 ± 30.7	<20	N/A	2.0mg/L
Coliform, MF fecal	N/A	SM 9222 D -1997	W	N/A	N/A	<20	N/A	1 cfu/100 ml
Coliform, MF total	N/A	SM9222 B -1997	W	N/A	N/A	<20	N/A	1 cfu/100 ml
Coliform, MPN fecal	N/A	SM 9221 B	W	N/A	N/A	<20	N/A	2 MPN/100 ml
Coliform, MPN total	N/A	SM9221 B- 2006	W	N/A	N/A	<20	N/A	2 MPN/100 ml
TOC	N/A	SM5310 B- 2000	W	80-120	90-110	<20	0.124mg/L	5 mg/L
Turbidity	N/A	SM 2130 B 2001	W	N/A	90-110	<20	N/A	1 NTU
Specific Conductance	N/A	SM 2510 B-1997	W	N/A	mfg	≤20	0.31	14.9 umhos/cm
Acidity to pH 4.5	N/A	SM 2310 B1997	W	N/A	mfg	≤20		1 mg/L
Acidity to pH 8.3	N/A	SM 2310 B1997	W	N/A	mfg	≤20		1 mg/L
Alkalinity to pH 8.3, total as $CaCO_3$	N/A	SM2320 B-1997	W	N/A	mfg	≤20		1 mg/L
Alkalinity to pH 4.5, total as $CaCO_3$	N/A	SM 2320 B 1997	W	N/A	mfg	≤20		1 mg/L

N/A = not applicable
mfg = Outside quality control standards are purchased and the manufacturer's published limits are used.

Table 5.4 EXAMPLES of QA Targets for WET CHEMISTRY Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL	PQL
Bromide	N/A	EPA 300.0 Rev. 2.1 1993 EPA 300.1-1 Rev. 1.0 1997	W	80-120	90-110	≤10	0.0363 mg/L	0.4 mg/L
Chloride	N/A	EPA 300.0 Rev. 2.1 1993 EPA 300.1-1 Rev. 1.0 1997	W	80-120	90-110	≤10	0.0869 mg/L	1.0 mg/L
Chlorophyll *a* (uncorrected)	N/A	EPA 445.0M Rev.1.2 1997	W	N/A	95-105	≤20	N/A	1 µg/L [1]
COD	N/A	Hach 8000 see footnote 14 in 40 CFR	W	85-115	85-115	≤20	4.0049 mg/L	20 mg/L
Color, ADMI	N/A	SM 2120 E-2001	W	N/A	85-115	≤20	1.1953 mg/L	10 c.u. [2]
Color, True	N/A	SM2120B-2001	W	N/A	85-115	≤20	1.7 c.u.	5 c.u.
Cyanide (Total)	SM4500-CN C 1999	EPA 335.4 Rev. 1.0 1993 QuikChem10-204-00-1-X	W	90-110	90-110	≤10	0.0057 mg/L	0.02 mg/L
Fluoride	N/A	EPA 300.0 Rev. 2.1 1993 EPA 300.1-1 Rev. 1.0 1997	W	80-120	90-110	≤10	0.0779 mg/L	0.40 mg/L
Formaldehyde	N/A	APHA, 1972 Method 111	W	80-120	85-115	≤20	0.1027 mg/L	0.2 mg/L
Grease & Oil	N/A	EPA 1664 A	W	78-114	78-114	<18	2.0024 mg/L	10 mg/L
	N/A	SW846-9071B	S	78-114	78-114	<18		1000 mg/Kg
Hexavalent Chromium	N/A	SM3500-Cr C-2009	W	80-120	85-115	≤20	9.5973 µg/L	5.0 µg/L
MBAS	N/A	SM5540 C-2000	W	85-115	85-115	≤20	0.087 mg/L	0.1 mg/L
Phenol	N/A	EPA 420.4 Rev. 1.0 1993 QuikChem10-210-00-1-A	W	90-110	90-110	≤10	1.32 µg/L	10 µg/L
Silica	N/A	SM 4500-SiO2 C-1997 QuikChem 10-114-27-1-A	W	90-110	90-110	≤10	0.0675 mg/L	2 mg/L
Sulfate	N/A	EPA 300.0 Rev. 2.1 1993 EPA 300.1-1 Rev. 1.0 1997	W	80-120	90-110	≤10	0.0783 mg/L	2 mg/L

Table 5.4 EXAMPLES of QA Targets for WET CHEMISTRY Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL	PQL
Sulfide	N/A	SM 4500-S_2 D-2000	W	90-110	85-115	≤20	0.0108 mg/L	0.1 mg/L
Total Dissolved Solids	N/A	SM2540 C 1997	W	N/A	85-115	5% of avg. weight	N/A	12 mg/L
Total residue	N/A	SM 2540 B-1997	W	N/A	85-115	5% of avg. weight	N/A	12 mg/L
Total volatile residue	N/A	SM 2540 E-1997	W	N/A	85-115	5% of avg. weight	N/A	12 mg/L
Total fixed residue		SM 2540 E-1997	W	N/A	85-115	5% of avg. weight	N/A	12 mg/L
Total Suspended Residue	N/A	SM2540 D-1997	W	N/A	85-115	5% of avg. weight	N/A	6.2 mg/L
Suspended Volatile Residue	N/A	SM 2540 E-1997	W	N/A	85-115	5% of avg. weight	N/A	6.2 mg/L
Suspended Fixed Residue		SM 2540 E-1997	W	N/A	85-115	<20*	N/A	6.2 mg/L

N/A = not applicable
[1] This is an estimated detection limit (EDL) - the minimum concentration of an analyte that yields a fluorescence 3X the fluorescence of blank filters which have been extracted according to the referenced method.
[2] c.u. = color units

Table 5.5 EXAMPLES of QA Targets for VOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
Dichlorodifluoromethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					20
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.31	2
Chloromethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					20
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.2	2
Vinyl Chloride	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					20
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.55	2
Bromomethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					20
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.24	2
Chloroethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					20
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.3	2
Trichlorofluoromethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					20
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.2	2
1,1-Dichloroethene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	$\leq$20	0.3	1
Methylene Chloride	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	$\leq$20	0.3	10
Trans-1,2-Dichloroethene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B REV. 2 1996 EPA 624	W				0.2	1
1,1 Dichloroethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10

Table 5.5 EXAMPLES of QA Targets for VOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
1,1 Dichloroethane	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B REV. 2 1996 EPA 624	W				0.2	1
2,2-Dichloropropane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.37	2
cis-1,2-Dichloroethene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.16	1
Chloroform	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.24	1
Bromochloromethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.31	1
1,1,1-Trichloroethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.18	1
1,1-Dichloropropene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.15	1
Carbon Tetrachloride	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.12	1
1,2-Dichloroethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.25	1
Trichloroethene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W					1

Table 5.5 EXAMPLES of QA Targets for VOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
1,2-Dichloropropane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.25	1
Bromodichloromethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260/624	W	70-130	70-130	≤20	0.26	1
Dibromomethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.45	1
cis-1,3-Dichloropropene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B REV. 2 1996 EPA 624	W				0.19	2
trans-1,3-Dichloropropene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.18	2
1,1,2-Trichloroethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.45	1
Tetrachloroethene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.08	1
1,3-Dichloropropane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.29	1
Dibromochloromethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.29	2
1,2-Dibromoethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					9
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.21	1

Table 5.5 EXAMPLES of QA Targets for VOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
Chlorobenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					9
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.15	1
1,1,1,2-Tetrachloroethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.15	1
Bromoform	EPA 5035 Rev.0 1996	EPA 8260	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.36	2
1,1,2,2-Tetrachloroethane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				1.52	5
1,2,3-Trichloropropane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.54	1
Bromobenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.33	1
2-Chlorotoluene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.18	1
4-Chlorotoluene	EPA 5030	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.18	1
1,3-Dichlorobenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.22	1

Table 5.5 EXAMPLES of QA Targets for VOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
1,4-Dichlorobenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.16	1
1,2-Dichlorobenzene	EPA 5035 REV.0 1996 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.23	1
1,2-Dibromo-3-Chloropropane	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				1.39	2
1,2,4-Trichlorobenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.2	1
Hexachlorobutadiene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.25	1
1,2,3-Trichlorobenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.29	1
Methyl-tert-butyl ether	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				1.72	5
Benzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.16	1
Toluene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.17	1
Ethyl benzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10

Table 5.5 EXAMPLES of QA Targets for VOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
Ethyl benzene	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W	70-130	70-130	≤20	0.1	1
m,p-Xylenes	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					20
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.23	2
o-Xylene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.11	1
Styrene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.14	1
Isopropylbenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.11	1
n-Propylbenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.13	1
1,3,5-Trimethylbenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.19	1
tert-Butylbenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.16	1
1,2,4-Trimethylbenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.18	1
sec-Butylbenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.12	1
p-isopropyltoluene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.16	1
n-Butylbenzene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10

Table 5.5 EXAMPLES of QA Targets for VOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				0.14	1
Naphthalene	EPA 5035 Rev.0 1996	EPA 8260B Rev. 2 1996	S					10
	EPA 5030B Rev.2 1996 EPA 624	EPA 8260B Rev. 2 1996 EPA 624	W				25	2
TPH-GRO	EPA 5030B Rev.2 1996	8015C Rev. 3 2007	W	80-120	80-120	≤40	0.02 mg/L	0.20 mg/L
	EPA 5035 Rev.0 1996	8015C Rev. 3 2007	S	80-120	80-120	≤40	2mg/kg	6mg/kg

Table 5.6 EXAMPLES of QA Targets for SEMIVOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
ANILINE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				260	660
PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	19 -49	20 - 41	≤42	3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	48 -98	37 - 76	≤35	260	660
BIS(2-CHLOROETHYL) ETHER	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2-CHLOROPHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	43 – 91	39 – 100	≤33	2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	47 – 96	35 – 94	≤50	130	660
1,3-DICHLOROBENZENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
1,4-DICHLOROBENZENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	32 - 109	41 - 92	≤22	2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	36 - 68	24 - 499	≤27	130	660
BENZYL ALCOHOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				4	30
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				260	1300
1,2-DICHLOROBENZENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2-METHYL PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
BIS(2-CHLOROISOPROPYL) ETHER	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
4-METHYL PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	41 - 116	48- 105	≤38		10

Table 5.6 EXAMPLES of QA Targets for SEMIVOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
N-NITROSO-DI-N-PROPYLAMINE	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	47 - 84	41 - 82	≤38	130	660
HEXACHLORO-ETHANE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
NITROBENZENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
ISOPHORONE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2-NITRO PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2,4-DIMETHYL PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625/8270	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				200	660
BENZOIC ACID	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				10	50
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				660	3300
BIS(2-CHLOROETHOXY) METHANE	EPA 625/3510	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2,4-DICHLORO PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
1,2,4-TRICHLORO-BENZENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	39 - 111	41 - 89	≤40	2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	45 – 76	33 - 78	≤23	130	660
NAPHTHALENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
4-CHLOROANILINE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				4	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				330	1300
	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10

Table 5.6 EXAMPLES of QA Targets for SEMIVOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
HEXACHLORO-BUTADIENE	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
4-CHLORO-3-METHYL PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	46 - 100	44 - 109	≤24	5	20
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	49 - 89	44 - 81	≤33	130	660
2-METHYL NAPHTHALENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
HEXACHLORO-CYCLOPENTADIENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				4	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2,4,6-TRICHLORO PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2,4,5-TRICHLORO PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2-CHLORO NAPHTHALENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625/8270	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2-NITROANILINE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				660	3300
DIMETHYL PHTHALATE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
ACENAPHTHYLENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2,6-DINITROTOLUENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
3-NITROANILINE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				4	50
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				660	3300
ACENAPHTHENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	46 - 118	42- 103	≤31	2	10

Table 5.6 EXAMPLES of QA Targets for SEMIVOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	53 - 87	40 - 80	≤19	130	660
2,4-DINITRO PHENOL	EPA 625/3510 EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				10	50
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				660	3300
4-NITRO PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	13 - 60	10 - 61	≤40	10	50
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	53 - 108	46 - 106	≤50	660	3300
DIBENZOFURAN	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
2,4-DINITROTOLUENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	38 - 121	46 - 109	≤38	3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	49 - 96	51 - 92	≤47	130	660
DIETHYL PHTHALATE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
4-CHLOROPHENYL PHENYL ETHER	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
FLUORENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				4	12
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
4-NITROANILINE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				10	50
	EPA 3550 EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				660	3300
4,6-DINITRO-2-METHYL PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				10	50
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				660	3300
N-NITROSODI-PHENYLAMINE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
4-BROMOPHENYL PHENYL ETHER	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
HEXACHLORO-BENZENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10

Table 5.6 EXAMPLES of QA Targets for SEMIVOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
PENTACHLORO- PHENOL	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	37 - 118	34 -122	≤45	10	30
	EPA 3550 Rev. 3 2007	EPA 8270 EPA 8270D Rev.4 2007	S	37 - 84	28 - 88	≤47	660	3300
PHENANTHRENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
ANTHRACENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
DI-N-BUTYL PHTHALATE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
FLUORANTHENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
PYRENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W	37 - 123	21 - 148	≤31	2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S	57 - 93	39 - 90	≤36	130	660
BUTYLBENZYL PHTHALATE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
3,3'-DICHLORO-BENZIDINE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				10	30
	EPA 3550	EPA 8270D Rev.4 2007	S				260	1300
BENZO(A)-ANTHRACENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550	EPA 8270D Rev.4 2007	S				130	660
CHRYSENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550	EPA 8270D Rev.4 2007	S				130	660
BIS(2-ETHYLHEXYL) PHTHALATE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10

Table 5.6 EXAMPLES of QA Targets for SEMIVOLATILES Accuracy, Precision and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
	EPA 3550C Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
DI-N-OCTYL PHTHALATE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				2	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
BENZO(B)-FLUORANTHENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
BENZO(K)-FLUORANTHENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
BENZO(A)PYRENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				3	10
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
INDENO(1,2,3-CD)-PYRENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				5	15
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
DIBENZO(A,H)-ANTHRACENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				5	15
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
BENZO(G,H,I)-PERYLENE	EPA 625 EPA 3510C Rev. 3 1996	EPA 625 EPA 8270D Rev.4 2007	W				5	15
	EPA 3550 Rev. 3 2007	EPA 8270D Rev.4 2007	S				130	660
TPH - DRO	EPA 3550 Rev. 3 2007	8015C Rev.3 2007	W	50 - 130	50 - 130	≤40	0.05 mg/L	0.5 mg/L
	EPA 3550 Rev. 3 2007	8015C Rev.3 2007	S	31 - 140	31 - 140	≤40	2 mg/Kg	10 mg/Kg

Table 5.7 EXAMPLES of QA Targets for CHLORINATED ACID HERBICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W = µg/L and S = µg/kg)	PQL (W = µg/L and S = µg/kg)
ACIFLUORFEN (BLAZER)	EPA515.1, 8151A	EPA 8151A, 8000B EPA 615	W				.04	0.30
	EPA515.1, 8151A	EPA 8151A, 8000B	S				.71	3.3
BENTAZON	EPA515.1, 8151A	EPA 8151A, 8000B	W				.05	0.40
	EPA515.1, 8151A	EPA 8151A, 8000B	S				.94	3.3
2,4-D	EPA515.1, 8151A	EPA 8151A, 8000B	W	30-142	30-142	≤35	.09	0.45
	EPA515.1, 8151A	EPA 8151A, 8000B	S	39-146	39-146	≤30	2.56	6.7
2,4-DB	EPA515.1, 8151A	EPA 8151A, 8000B	W				.23	2
	EPA515.1, 8151A	EPA 8151A, 8000B	S				3.9	27
DICAMBA	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.07	0.2
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				1.2	3.3
3,5-DICHLOROBENZOIC ACID	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.1	0.20
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				1.16	3.3
DICHLORPROP	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.11	0.60
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				6.38	20
DINOSEB	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.08	0.60
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				2.02	6.7
4-NITROPHENOL	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.21	0.60
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				NE	13
PENTACHLORO-PHENOL (PCP)	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.05	0.10
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				.7	3.3
2,4,5- T	EPA 515.1, 8151A	EPA 8151A, 8000B	W	30-131	30-131	≤26	.04	0.20
	EPA 515.1, 8151A	EPA 8151A, 8000B	S	23-143	23-143	≤30	.87	3.3
2,4,5-TP (SILVEX)	EPA 515.1, 8151A	EPA 8151A, 8000B	W	41-117	41-117	≤21	.04	0.20
	EPA 515.1, 8151A	EPA 8151A, 8000B	S	10-134	10-134	≤30		

Table 5.8 EXAMPLES of QA targets for ORGANOCHLORINE PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W= µg/L and S= µg/kg)	PQL (W = µg/L and S = µg/kg)
ALACHLOR	EPA 3510C Rev. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.15	0.50
	EPA 3550C	EPA 8081B REV. 2 2007	S				5.33	32
ALDRIN	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W	50-98	50-98	≤20	0.01	.03
	EPA 3550C	EPA 8081B REV. 2 2007	S	42-128	42-128	≤30	0.67	2
BHC-ALPHA	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	.03
	EPA 3550C	EPA 8081B REV. 2 2007	S				0.67	2
BHC-BETA	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	.03
	EPA 3550	EPA 8081B REV. 2 2007	S				0.67	2
BHC-DELTA	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	.06
	EPA 3550C	EPA 8081B REV. 2 2007	S					4
BHC-GAMMA (LINDANE)	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W	56-106	56-106	≤20	0.01	.03
	EPA 3550C	EPA 8081B REV. 2 2007	S	59-123	59-123	≤30	0.67	2
CHLORDANE, TECHNICAL	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				NE	0.50
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				NE	30
CHLORDANE-ALPHA	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
CHLORDANE-GAMMA	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
CHLORDENE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.33	2
CHLORONEB	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.1	0.3
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				3.33	20
CHLOROBENZILATE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.16	0.50
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				6.33	38

Table 5.8 EXAMPLES of QA targets for ORGANOCHLORINE PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W= µg/L and S= µg/kg)	PQL (W = µg/L and S = µg/kg)
CHLOROTHALONIL	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.06	0.20
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				NE	13
DCPA	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				.67	2
DDD, OP	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.02	0.06
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	4
DDD, PP	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
DDE, OP	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.05
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				1.33	8
DDE, PP	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
DDT, OP	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W					0.05
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
DDT, PP	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W	53-111	53-111	≤27	.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S	35-134	35-134	≤30	0.67	2
DIELDRIN	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W	52-118	27-149	≤20	.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S	42-134	54-127	≤30	0.67	2
ENDOSULFAN I	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
ENDOSULFAN II	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
ENDOSULFAN SULFATE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				.03	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
ENDRIN	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W	56-121	47-117	≤20	.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S	42-139	44-120	≤30	0.67	2

Table 5.8 EXAMPLES of QA targets for ORGANOCHLORINE PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W= µg/L and S= µg/kg)	PQL (W = µg/L and S = µg/kg)
ENDRIN ANDEHYDE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
ENDRIN KETONE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
ETHAZOLE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.03	0.09
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				3	20
HEPTACHLOR	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W	55-107	55-107	≤20	.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S	65-139	65-139	≤30	0.67	2
HEPTACHLOR EPOXIDE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
HEXACHLOROBENZENE (HCB)	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.33	2
METHOXYCHLOR	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	2
MIREX	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				1	6
TRANS-NONACHLOR	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.05
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	6
OXYCHLORDANE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.02	0.06
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	4
MIXED-PERMETHRIN	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.40	1.20
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				21	130
PROPACHLOR	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.20	0.60
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				6.67	40
TECNAZENE	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	0.03
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.33	2

Table 5.8 EXAMPLES of QA targets for ORGANOCHLORINE PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (W= µg/L and S= µg/kg)	PQL (W = µg/L and S = µg/kg)
TRANS NONACHLOR	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.01	.05
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				1	6
TRIFLURALIN	EPA 3510C REV. 3 1996	EPA 608 EPA 8081B REV. 2 2007	W				0.02	0.06
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				0.67	4
AROCHLOR 1016	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W	70-150	70-150	≤20	0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S	70-150	70-150	≤30	22	66
AROCHLOR 1021	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W				0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S				22	66
AROCHLOR 1032	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W				0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S				22	66
AROCHLOR 1042	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W				0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S				22	66
AROCHLOR 1048	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W				0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S				22	66
AROCHLOR 1054	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W				0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S				22	66
AROCHLOR 1260	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W	70-150	70-150	≤20	0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S	70-150	70-150	≤30	22	66
AROCHLOR 1262	EPA 3510C REV. 3 1996	EPA608 EPA 8082A REV. 1 2007	W				0.20	1.0
	EPA 3550C REV. 3 2007	EPA 8082A REV. 1 2007	S				22	66
TOXAPHENE	EPA 3510C REV. 3 1996	EPA608 EPA 8081B REV. 2 2007	W				NE	3.0
	EPA 3550C REV. 3 2007	EPA 8081B REV. 2 2007	S				NE	200

Table 5.9 EXAMPLES of QA targets for ORGANONITROGEN PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S=ug/Kg)	PQL (W=µg/ and S=ug/Kg)
AMETRYN	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.6	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
ATRATON	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.6	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
ATRAZINE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.7	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
BROMACIL	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				6.8	15
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
BUTACHLOR	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				7.2	25
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
BUTYLATE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				3.5	10
CHLORPROPHAM	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				9.2	30
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
CYANAZINE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.5	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
CYCLOATE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				4.3	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150

Table 5.9 EXAMPLES of QA targets for ORGANONITROGEN PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S=ug/Kg)	PQL (W=µg/ and S=ug/Kg)
DIPHENAMID	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W	61 - 107	61 - 107	11	1.6	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S	70 - 130	70 - 130	30		500
EPTC (EPTAM)	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				2.4	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
FENARIMOL	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				2.5	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
FLURIDONE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				20	80
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
HEXAZINONE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				3.2	10
	EPA 3550C REV. 3 2007	EPA 8141Rev. 2 2007	S					500
METHYL PARAOXON	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				4	15
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
METOLACHLOR	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				10	25
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
METRIBUZIN	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W					30
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					1000

Table 5.9 EXAMPLES of QA targets for ORGANONITROGEN PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S=ug/Kg)	PQL (W=µg/ and S=ug/Kg)
MOLINATE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				2.4	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
NAPROPAMIDE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				2.3	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
NORFLURAZON	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				3.6	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
PEBULATE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				2.2	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
PROMETON	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.6	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
PROMETRYN	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.6	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
PRONAMIDE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				6.4	20
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
PROPAZINE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.7	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150

Table 5.9 EXAMPLES of QA targets for ORGANONITROGEN PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision %RPD	MDL (W = µg/L and S=ug/Kg)	PQL (W=µg/ and S=ug/Kg)
SIMETRYN	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.7	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
TEBUTHIURON	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				6.6	20
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					500
TERBACIL	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				7.7	20
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					1000
TERBUTRYN (PREBANE)	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W	64 - 117	64 - 117	11	1.6	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S	70-130	70-130	30		500
TRIADIMEFON	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				1.9	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					
TRICYCLAZOLE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				15	30
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					
TETRACHLOVINPHOS	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W				3	5
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S					150
VERNOLATE	EPA 3510C REV. 3 1996	EPA 619 EPA 8141 Rev. 2 2007	W	69-110	69-110	10	2.3	10
	EPA 3550C REV. 3 2007	EPA 8141 Rev. 2 2007	S	70-130	70-130	30		150

* = Interim values

Table 5.10 EXAMPLES of QA targets for ORGANOPHOSPHORUS PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision% RPD	MDL (W =µg/L and S=ug/Kg)	PQL (W=µg/ and S=ug/Kg)
CARBOPHENOTHION	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.22	1
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				15	70
CHLORPYRIFOS	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.1	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				7	35
DEF	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.1	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				7	35
DEMETON	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.35	1
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				23	70
DIAZINON	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W	62-98	62-98	≤18	0.1	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S	65 -130	65 -130	≤30	7	35
DICHLORVOS	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.17	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				11	35
DIMETHOATE	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.17	1
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				11	70
DISULFOTON	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.28	1
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				19	70
DISULFOTON SULFONE	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				NE	0.4
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				NE	33
DISULFOTON SULFOXIDE	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				NE	10
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				NE	NE

Table 5.10 EXAMPLES of QA targets for ORGANOPHOSPHORUS PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision% RPD	MDL (W =µg/L and S=ug/Kg)	PQL (W=µg/ and S=ug/Kg)
EPN	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W	62-113	62-113	≤17	0.12	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S	69-130	69-130	≤30	4	35
ETHION	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.1	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				6	35
ETHOPROP	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.13	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				9	35
FENTHION	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.13	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				9	35
FENSULFOTHION	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				35	130
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				5.5	16
MALATHION	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.18	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				12	35
MEVINPHOS	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.29	1
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				19	70
MONOCROTOPHOS	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				NE	1
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				NE	33
NALED	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.78	2.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				52	170
ETHYL PARATHION	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.18	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				12	35

Table 5.10 EXAMPLES of QA targets for ORGANOPHOSPHORUS PESTICIDES Accuracy, Precision, and MDLs/PQLs
[Current limits can be found in unit QC log book or QC documents]

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision% RPD	MDL (W =µg/L and S=ug/Kg)	PQL (W=µg/ and S=ug/Kg)
METHYL PARATHION	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.15	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				10	35
PHORATE	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.19	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				13	35
RONNEL	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W	69 - 114	69 - 114	≤16	0.17	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S	69 - 130	69 - 130	≤30	11	35
SULFOTEPP	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.13	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				9	35
TERBUFOS	EPA 3510C REV. 3 1996	EPA 614 EPA 8141 REV. 2 2007	W				0.19	0.5
	EPA 3550C REV. 3 2007	EPA 8141 REV. 2 2007	S				13	35

6.0 Sampling Procedures

The DWR Water Sciences Section Chemistry Laboratories do not provide field sampling services. Other Divisions, Branches and Sections have their own SOPs/QAM for field sampling protocol [For example, the Ecosystems Branch SOP can be found at: http://portal.ncdenr.org/web/wq/ess/eco/ams]. The Chemistry Laboratories' responsibilities in the sample collection process lies in supplying the sampler with proper containers and preservatives and verifying proper sample handling upon receipt. The Water Sciences Section Chemistry Laboratories welcome consultation with collectors for whatever assistance can be provided.

6.1 Sampling Containers

6.1.1 Sampling Container Sources

The Water Sciences Section Chemistry Laboratory offers pre-cleaned sampling containers for use by laboratory field sampling personnel. Some sampling containers are purchased from reputable manufacturers and are certified as cleaned according to EPA specifications (*Specifications and Guidance for Contaminant-Free Sample Containers*, OSWER Directive #9240.0-05A, December, 1992). When commercial pre-cleaned containers are not available, the procedures outlined in Analytical Procedure Table 8-1 are followed.

Examples of sources for all bottles are:

(a) Daniel's Scientific - variety of inorganic analyses Eagle Picher or ESS - VOA
(b) Fisher/VWR - BOD, Coliform, Chlorophyll *a*, Cyanide Nalgene bottles
(c) Qorpak - Total Phenol
(d) QEC - Pesticides, SVOA, Oil & Grease (sometimes I-Chem) sediments

6.1.2 Types of Bottles:

The types of bottles utilized are:

(a) 500 mL disposable plastic bottles (juice bottles)
(b) 1000 mL, 250 mL plastic bottles
(c) 4000 mL amber glass bottles with Teflon-lined caps
(d) 125 mL, 250 mL, 1000 mL glass jar with Teflon-lined caps
(e) 40 mL clear and amber VOC vial with Teflon/silicon septum
(f) 1000 mL brown plastic bottles
(g) 1000 mL wide-mouth glass bottles with Teflon-lined caps

6.1.3 Bottle Testing – 500 mL Disposable Plastic Bottle Testing

The 500 mL disposable plastic bottles (i.e., Daniel's Scientific bottles) must be checked for interfering contaminants. Bottles are tested at least twice per year and whenever a new vendor is used. Bottles must be tested prior to being placed into use. The QA/QC Coordinator maintains documentation of the process. Documentation includes: lab number, container, vendor, lot number, QA number, date received at lab, final report date, date of initial shipment to collector, pass/fail results and actions taken. The 500ml bottles are checked for the following contaminants.

- Chemical Oxygen Demand
- Total Residue
- Alkalinity
- Total Organic Carbon
- Turbidity
- Anions – Bromide, Chloride, Fluoride and Sulfate
- Metals, including Boron
- Nutrients – Ammonia, Nitrate+Nitrite, Total Phosphorous

Reusable containers will also be tested once or twice per year for contamination following the same procedure outlined above. Only 1000 mL plastic amber bottles, 1000 mL glass bottles, 1000 mL plastic bottles, and 250 mL plastic bottles are cleaned and reused. In order to certify that the re-used containers are clean, random bottles are periodically analyzed for the target constituent when controls are not built into the analytical process. An outline of the cleaning procedures can be found in Analytical Procedures Table 8-1. The cleaned bottles are stored in the Sample Shipping/Receiving area (G-098) of the laboratory away from laboratory activities.

Note: Approximately once a month, 250 mL plastic fecal bottles are randomly tested for contamination from each sterilized batch. Please refer to Microbiology SOP for the Analysis of Fecal Coliform.

6.1.4 Certified Containers Testing

A baseline for certified containers (such as 40 ml VOA vials for volatiles and sulfide analyses) will be established by the procedure described in Section 6.1.3. Certified containers will be tested periodically or when a new vendor or bottle type is used.

6.1.5 Non Certified Containers Testing

A baseline for non-certified containers (such as 1 liter jugs for Pesticides and Semivolatile analyses) will be established by the procedure described in Section 6.1.3 Bottle Testing. Non Certified containers will be tested when a new vendor or bottle type is used.

6.2 Preservatives

Upon request, preservatives are provided to field sampling personnel in bottles or in sealed pre-scored ampoules. Preservatives from new lots, such as Nitric Acid, a preservative for metals testing, are tested for contamination prior to shipping. Test results are logged into a spreadsheet by unit supervisor.

In some cases, preservatives supplied directly from a private vendor are drop-shipped to the regional offices. The sodium thiosulfate and EDTA preservatives for coliform samples are prepared in the Microbiology Unit and delivered to the Support Unit. The sodium thiosulfate and EDTA preservatives are then added to the microbiology sample containers. Whether prepared by the laboratory or bought pre-preserved, the grades of the preservatives are, at a minimum:

- Nitric Acid - ACS grade or equivalent
- Sodium Bisulfate - ACS grade or equivalent
- Sodium Hydroxide - ACS grade or equivalent
- Sulfuric Acid - ACS grade or equivalent
- Sodium Thiosulfate - ACS grade or equivalent
- Ascorbic Acid - ACS grade or equivalent
- Zinc Acetate - ACS grade or equivalent
- Phosphoric Acid - ACS grade or equivalent
- Ferrous Ammonium Sulfate - ACS grade or equivalent
- Hydrochloric Acid – ACS grade or equivalent
- EDTA – ACS grade or equivalent

The Water Sciences Section Chemistry Laboratory also provides the following supplies used during sample collection activities:

- Security seals
- Total residual chlorine test strips
- Wide range pH test strips
- Narrow range pH test strips

6.3 Reuse of Bottles and Bottle Cleaning

Only 1000 mL plastic amber bottles, 1000 mL glass bottles, 1000 mL plastic bottles, and 250 mL plastic bottles are cleaned and reused. In order to certify that the re-used containers are clean, random bottles are periodically analyzed for the target constituent when controls are not built into the analytical process. An outline of the cleaning procedures can be found in Analytical Procedures Table 8-1. The cleaned bottles are stored in the Sample Shipping/Receiving area (G-098) of the laboratory away from laboratory activities in a cabinet with lids secured.

The following parameters utilize bottles that are cleaned and reused:

- Chlorophyll-a
- BOD
- Coliform
- Phenol

6.4 Sampling Containers, Preservatives and Holding Times

The sampling container types, preservation techniques and holding times for the parameters analyzed by the laboratory are summarized in Tables 6.1 (Water Sciences Section Water Quality) and 6.2 (Water Sciences Section Groundwater). These tables are adapted from *40 CFR, Chapter 1, Part 136, Table II*; however, any time there is a federal register update, lab procedures will follow the updated protocol. The QAO has a licensed copy of ASTM D7365-09a, which details sampling, preservation and mitigating interferences in water samples for analysis of Cyanide. Special attention should be paid to the footnotes for any deviations. The information for soil/sediment samples is adapted from *Test Methods for Evaluating Solid Waste, SW-846, Revision IV*. Tissue samples are collected, filleted and frozen in metal tins prior to submission to the laboratory. Tissue samples are frozen up to one year until analysis.

If the container, preservative or holding time requirements are not met for a sample, the sample may be rejected by the laboratory or the reports will be qualified using a data qualifier code and accompanied by a Sample Condition Upon Receipt (SCUR) report, Sample Anomaly Report (SAR) or Sample Comments on the final report. If criteria are not specified in a source document, internal DWR Water Sciences Section guidelines will be used. These guidelines are footnoted in Tables 6.1 and 6.2.

The Water Sciences Section Chemistry Laboratories do not perform field analyses.

6.4.1 Definition of Holding Time

The date and time of sampling documented on the field sheet establishes the date and time zero. For composite samples, the date and time the 24-hour compositing cycle ended establishes the date and time zero. When the maximum allowable holding time is expressed in days, the holding time is based on day measured. Holding times, expressed in 72 hours or less, are measured from date and time zero. The first day of holding time ends twenty-four hours after sampling. Holding times for analyses include preparation, quantitation and any necessary reanalysis except as noted below.

6.4.1.1 SVOA/Pesticides

Holding times for sample preparation for semi-volatile organics are measured from the date and time of sampling until the solvent contacts the sample. If a sample is to be extracted on the day of expiration, the actual time of extraction must be recorded on the sample preparation worksheet. Holding times for analysis are measured from the date and time of initiation of extraction to the time of injection into the gas chromatograph.

6.4.1.2 VOA

Holding times for volatile organics are measured from the date and time of sampling to the date and time of injection into the gas chromatograph. The time of initiation of purging is considered the injection time, but data systems record the start of the chromatographic run rather than the start of purging. Hence, if a sample is so near expiration that the start-of-purging time rather than the chromatographic run time is needed to document the integrity of the sample, the analyst must record

the start-of-purging time in the instrument log or be able to back calculate the start-of-purging time based on the purge time recorded in the instrument method files.

6.4.1.3 Inorganics and Metals

For inorganics and metals analysis, the preparation/digestion/distillation must be started in time to allow the analysis step to be initiated as documented in the instrument log, instrument output, or analysis worksheet, within the maximum allowable holding time as measured from the sampling date and time.

6.4.1.4 Microbiologicals

For microbiological analyses such as coliform and BOD, the holding time is measured from the date and time of sampling to the date and time when filtration and incubation begins, respectively.

6.5 Scheduling Laboratory Capacity

Major sampling events must be scheduled with the laboratory prior to formal acceptance of the samples by the laboratory. Samples are accepted for analysis by logging them into DWR LABWORKS™ LIMS. Field sheets, SCURs, and final reports are also scanned into Laserfiche®. The supervisors are responsible for scheduling samples by assessing the capacity and previously scheduled workload of the laboratory and makes decisions regarding work assignments whenever laboratory capacity for any work group may be exceeded.

6.6 Processing Time-Sensitive Samples

With a continuing focus on data quality assurance, staffing and scheduling constraints, the Laboratory has provided the following guidance on the submission of time-sensitive samples in Tables 6.1 and 6.2, as well as, on the Water Sciences Section website. http://portal.ncdenr.org/web/wq/lab/ops/samples#Time_Sensitive_Samples

In order to properly process samples and keep overtime to a minimum, the following limitations on submission of these analyses should be observed. Should emergencies arise, sample collectors have been instructed to call the appropriate analytical Branch Head.

- *Samples for Chlorophyll a, BOD_5, PO_4, Turbidity, Color: ADMI and Platinum Cobalt (PtCo), MBAS, NO2-Nitrite; NO3-Nitrate (unless as NO3NO2), hexavalent chromium, Fecal Coliform and Total coliform analysis will not be accepted after 3:00 PM Monday thru Thursday and 1:00 PM on Fridays.*
- *Samples for PO_4, Color: ADMI and Platinum Cobalt (PtCo), MBAS, NO2-Nitrite; NO3-Nitrate (unless as NO3NO2), hexavalent chromium, Fecal Coliform and Total coliform analysis will not be accepted on a workday that immediately precedes a holiday or holiday weekend.*
- *Samples for BOD_5 will not be accepted on work days that would result in the five day test ending on a Holiday or Holiday weekend.*
- *Samples for Chlorophyll a and Turbidity may be submitted for analysis until 1:00 P.M. on a workday that immediately precedes a holiday or holiday weekend.*
- *Staff planning to submit more than five samples for these parameters should contact the laboratory to schedule these samples in advance. If fewer than five samples are to be submitted for these parameters, we ask that you please simply notify the laboratory that short hold samples are coming 48 hours prior to submitting whenever possible.*
- *Coliform bacteria samples that need to meet the eight-hour holding time required by the Clean Water Act will not be accepted after 3:00 PM on normal Monday through Thursday workdays. (Please have samples to lab within 6 hours to meet the CWA holding time)*
- *All tube coliform samples must be scheduled in advance by contacting the Bio/Metals Unit Supervisor or the Microbiology Unit Lead Chemist.*
- *Unpreserved samples for individual analysis of nitrate or nitrite should be scheduled with the Nutrients/ Wet Chemistry Unit Supervisor or the Nutrients group prior to submittal. With 48-hour hold times for these samples, analytical runs need to be specially scheduled to accommodate these samples. NOTE: A concurrent preserved nutrients sample should be submitted for which nitrate+nitrite analysis has been requested.*

The Asheville Regional Laboratory has provided the following guidance on submission of time-sensitive samples**.**

- *Samples for BOD, Turbidity, and MF coliform analysis will not be accepted after 3:00 PM on Fridays or workdays that immediately precede a holiday. Staff planning to submit more than three samples on these days for these parameters should contact the laboratory to schedule these samples in advance.*
- *Coliform bacteria samples that need to meet the eight-hour holding time required by the Clean Water Act will not be accepted after 4:00 PM on normal Monday through Thursday workdays. (Please have samples to lab within 6 hours to meet the CWA holding time)*
- *All tube coliform samples must be scheduled in advance by contacting the laboratory.*

The web site also offers up-to-date guidance for specific limitations on sample submission established to allow Water Sciences Section Chemistry Laboratory staff to observe state holidays. http://www.ncdenr.gov/web/wq/lab/ops/sample

Table 6.1. Required Containers, Preservation Techniques and Holding Times (Surface Water Samples)

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COLLECTION AND PRESERVATION OF SURFACE WATER SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Reference: 40 CFR Part 136.3 Table II

Listed below is information on the collection and preservation of samples. The amount of sample listed is for average conditions; therefore, if you suspect that unusual conditions or interferences exist, please submit double the amount of sample. **Excluding purgeable organics and sulfide**, a one-half inch air space should be left in all bottles to allow for mixing before analysis. **When submitting a filtered sample, write "DIS" (for dissolved) in the box beside the parameter(s) on the field sheet.**

NPDES, Appendix A, Federal Register, 38, No. 75, Pt II. NOTE: All other organics will be analyzed using methods from the Federal Register, 40 CFR Part 136 when available and Solid Waste 846 methods. The Branch Supervisor must approve methods from any other source.

Samples must be shipped to the Laboratory as soon as possible after collection. Reference: 40 CFR Part 136.3 Table II				
Parameter[1]	**Minimum Required Volume**	**Container**[13] **P-Plastic G-Glass**	**Preservation**[20]	**Maximum Holding Time**[21]
Microbiology Parameters:				
Acidity	200 ml	P (disposable)	Cool ≤ 6ºC[24]	14 days
Alkalinity • includes bicarbonate & carbonate	200 ml	P (disposable)	Cool ≤ 6ºC[24]	14 days
BOD, 5-day	1 liter	P	Cool ≤ 6ºC[24]	48 hours[2]
CBOD, 5-Day	1 liter	P	Cool ≤ 6ºC[24]	48 hours[2]
Coliform: Fecal, Total, *E. coli* and Enterococci	250 ml (**each)**	P[3] (sterile)	Cool <10ºC 0.008% $Na_2S_2O_3$(0.1ml 10% $Na_2S_2O_3$/125 ml) and 15% EDTA[3]	6 hours[4]
Specific Conductance	200 ml	P (disposable)	Cool ≤6°C[24]	28 days
TOC	500 ml	P (disposable)	H_3PO_4 to pH<2; Cool ≤ 6ºC[24]	28 days
DOC	500 ml Include a Field Blank with DOC samples	P (disposable)	Field filter using 0.45um pore size; H_3PO_4 to pH<2	28 days

			Cool ≤ 6ºC[24]	
COLLECTION AND PRESERVATION OF SURFACE WATER SAMPLES FOR THE NC DWR WATER SCIENCES SECTION Reference: 40 CFR Part 136.3 Table II				
Parameter[1]	**Minimum Required Volume**	**Container**[13] **P- Plastic G- Glass**	**Preservation** [20]	**Maximum Holding Time** [21]
Turbidity	200 ml	P disposable)	Cool ≤ 6ºC[24]	48 hours[2]
Wet Chemistry Parameters:				
Bromide Chloride Fluoride Sulfate	500 ml	P (disposable)	Cool ≤ 6ºC[24]	28 days
Chlorophyll *a*[10]	500 ml	P (Brown wide-mouth)	Cool ≤ 6º C[24] - if filtered in field, store filters in the dark.	Filter within 24 hours 21 days (after filtration)
Color: ADMI	400 ml	P (disposable)	Cool ≤ 6º C[24]	48 hours[2]
Color: Platinum Cobalt	400 ml	P (disposable)	Cool ≤ 6º C[24]	48 hours[2]
COD	200 ml	P (disposable)	25% H_2SO_4 to pH<2; Cool ≤ 6ºC[24]	28 days
Cyanide, Total[27]	2 liters (2 x 1-liter bottles)	P	Add 0.6 g ascorbic acid[6], 6N NaOH to pH >10, not exceeding a pH of 11; Cool ≤6°C[24]	14 days[18]
Formaldehyde	500 ml	P (disposable)	Cool ≤6°C[24]	NA
Hexavalent Chromium	400 ml	P (disposable)	Cool ≤6°C[24], pH=9.3-9.7	24 hours (notify lab of collection)
MBAS	500 ml	P (disposable)	Cool ≤ 6º C	48 hours[2] (notify lab of collection)

COLLECTION AND PRESERVATION OF SURFACE WATER SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Reference: 40 CFR Part 136.3 Table II

Parameter[1]	**Minimum Required Volume**	**Container**[13] **P – Plastic G – Glass**	**Preservation**[20]	**Maximum Holding Time**
Oil & Grease, HEM	2 liters (2 x 1-liter bottles) (17)	G (wide-mouth quart jar w/ Teflon-lined cap)	1:1 H_2SO_4 to pH<2; Cool ≤6°C[24]	28 days
Phenols, Total recoverable	2 liters (2 x 1-liter bottles)	G (Phenol Bottle) only	1:1 H_2SO_4 to pH <2 (1 ml of Ferrous Ammonium Sulfate if sample contains oxidizer); Cool ≤6°C[24]	28 days
Residue, Suspended -Suspended Solids (plus Volatile/Fixed, if requested)	500 ml[25]	P (disposable)	Cool ≤ 6ºC[24]	7 days
Residue, Total -Total Solids (plus Volatile/Fixed, if requested)	500 ml[25]	P (disposable)	Cool ≤ 6ºC[24]	7 days
TDS -Total Dissolved Solids	500 ml[25]	P (disposable)	Cool ≤ 6ºC[24]	7 days
Sulfide	120 ml (40-ml x 3)[9]	G 40-ml VOA vials with Teflon-lined septum	Add 1 ml of 2N zinc acetate plus 6 N NaOH to pH>9; Cool ≤6°C[24] -leave no headspace in bottle.	7 days
Tannin and Lignin	500 ml	P (disposable)	Cool ≤6°C[24]	28 days
Other Parameters:				
pH (5)	Lab analysis inappropriate; analyze in field within 15 minutes of sample collection.			

COLLECTION AND PRESERVATION OF SURFACE WATER SAMPLES FOR THE NC DWR WATER SCIENCES SECTION
Reference: 40 CFR Part 136.3 Table II

Parameter[1]	**Minimum Required Volume**	**Container**[13] **P – Plastic G - Glass**	**Preservation** [20]	**Maximum Holding Time**
Hardness, Total -request by checking Hardness, Total as CaCO3, or Ca and Mg, on field sheet. -Can be part of metals sample) Total Hardness=2.497[Ca mg/L]+4.118[Mg mg/L]	500 ml	P (disposable)	1+1 HNO_3 to pH<2	6 months
Parameter[1]	Minimum Required Volume	Container[13] P – Plastic G – Glass	Preservation [20]	Maximum Holding Time
Nutrients Parameters:				
Ammonia (NH3-N)	500 ml (1 bottle for all, except when chlorine present; then include additional bottle of de-chlorinated sample for NH3-N)	P (disposable)	25% H_2SO_4 to pH<2[7] Cool ≤6°C[24] 0.008% $Na_2S_2O_3$ to de-chlorinate (See note 11)	28 days
Nitrate-Nitrite (NO3+NO2 – N)				
Total Kjeldahl Nitrogen (TKN)				
Total Phosphorus (TP)				
Dissolved Nutrients (4 parameters above)	200 ml (1 bottle)	P (disposable)	Field filter using 0.45um pore size; 25% H_2SO_4 to pH<2[7] ; Cool ≤6°C[24]	28 days

COLLECTION AND PRESERVATION OF SURFACE WATER SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Reference: 40 CFR Part 136.3 Table II

Parameter[1]	**Minimum Required Volume**	**Container**[13] **P – Plastic G – Glass**	**Preservation** [20]	**Maximum Holding Time** [21]
Nitrite (NO_2- N)	200 ml	P (disposable)	Cool ≤6°C[24]	48 hours[2] (notify lab of collection)
Nitrate (NO_3-N)	Calculated value using analytical results for NO3+NO2-N and NO2-N; submit samples for NO3+NO2-N and NO2-N			
Orthophosphate (PO_4-P)	200 ml	P (disposable)	Field filter within 15 minutes using 0.45 um pore size; Cool ≤6°C[24]	48 hours[2] (notify lab of collection)
Parameter[1]	Minimum Required Volume	Container P – Plastic G – Glass	Preservation [20]	Maximum Holding Time[21]
Metals Parameters:				
Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn, and Hg[19,]	500 ml (1 bottle)	P (disposable)	1+1 HNO3 to pH<2[26]	6 months (28 days for Mercury)
Boron	500 ml	P (disposable)	1+1 HNO3 to pH<2[26]	6 months
Mercury EPA 1631 E Hg (trace-level total Hg)	500 ml of sample; Plus a Field Blank must accompany each trace-level Hg sample	G (borosilicate), Teflon-lined cap	None required for total and dissolved Mercury – Use clean sampling techniques as described in EPA Method 1669.	28 days until preservation with BrCl[22] if the sample is oxidized in the sample bottle. Preserved samples are stable for up to 90 days from collection.

COLLECTION AND PRESERVATION OF SURFACE WATER SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Reference: 40 CFR Part 136.3 Table II

Parameter[1]	**Minimum Required Volume**	**Container**[13] **P – Plastic G – Glass**	**Preservation** [20]	**Maximum Holding Time**
Organics Parameters:				
Acid Herbicides	4 liters[8]	G (amber), Teflon-lined cap	Cool ≤6°C[24], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction[15] , 40 days after extraction
Pesticides -Organochlorine -Organonitrogen -Organophosphorus	4 liters[8]	G (amber), Teflon-lined cap	Cool ≤6°C[24], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction[15] 40 days after extraction
PCBs (polychlorinated biphenyls)	4 liters[8] (can be same bottle as for Pesticides)	G (amber), Teflon-lined cap	Cool ≤6°C[24], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction[15] 40 days after extraction
Semi-Volatile Organics (Base/Neutral & Acid Extractables)	4 liters[8]	G (amber), Teflon-lined cap	Cool ≤6°C[24], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction 40 days after extraction
TPH Diesel Range (aqueous)	4 liters[8]	G (amber), Teflon-lined cap	Cool ≤6°C[24], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction 40 days after extraction
Parameter[1]	Minimum Required Volume	Container P – Plastic G – Glass	Preservation [20]	Maximum Holding Time[21]
Volatile Organics (VOA)	40 ml x 4[9] A Trip blank (3 vials) must accompany all VOA samples	G, VOA vials, Teflon-lined septum	Cool ≤6°C[24], 0.6g Ascorbic Acid, or 0.008% $Na_2S_2O_3$ [11] HCl to pH 2[14,16] Leave no headspace in bottle.	14 days (7 days for aromatics only when unpreserved)
TPH Gasoline Range (aqueous)	40 ml x 4[9] A Trip blank (3 vials) must accompany all VOA samples.	G, VOA vials, Teflon-lined septum	Cool ≤6°C[24], 0.6g Ascorbic Acid 0.008% $Na_2S_2O_3$[11] HCl to pH 2 [14,16]	14 days

COLLECTION AND PRESERVATION OF SURFACE WATER SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

(SOIL & SEDIMENT SAMPLES)

******WHEN SUBMITTING SOIL AND SEDIMENT SAMPLES FOR ANALYSIS, A SEPARATE SAMPLE CONTAINER MUST BE COLLECTED FOR EACH OF THE ANALYTICAL GROUPS LISTED BELOW:

Parameter	Minimum Required Volume	Container[13] P-Plastic G-Glass	Preservation[20]	Maximum Holding Time[21]
Oil and Grease	8 oz. jar	G, Teflon-lined cap	1 ml of concentrated HCl per 100 grams soil to pH < 2; Cool ≤6°C	as soon as possible
Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sn, Se, Tl, V, Zn and Hg	8 oz. jar	G, Teflon-lined cap	Cool ≤6°C	refer to aqueous
Pesticides & PCBs (OC/ON/OP)	8 oz. jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; analyze w/in 40 days
Acid Herbicides	8 oz. jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; analyze w/in 40 days
Semi-Volatile Organics (BNAs)	8 oz. jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; analyze w/in 40 days
Volatile Organics (VOA)	4 oz. jar + trip blank	G, Teflon-lined cap or septum	Cool ≤6°C	14 days
TPH Gas Range (soil)	4 oz. jar + trip blank	G, Teflon-lined cap or septum	Cool ≤6°C	14 days
TPH Diesel Range (soil)	8 oz. jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; Analyze w/in 40 days

(1)Parameters grouped together e.g. Nutrients, may be submitted in the same bottle.
(2)48 hours is the maximum holding time, however, samples should be submitted to the Lab as soon as possible.
(3)Use the 250 ml wide-mouth sterile plastic bottles for all samples. All bottles contain sodium thiosulfate and EDTA reagents and should not be rinsed prior to sample collection.
(4)Litigation samples must be delivered to the laboratory within 6 hours of sample collection to meet 8 hour hold time.
(5) pH analysis must be performed on site.
(6)Add 0.6 g of ascorbic acid only if sample contains residual chlorine.
(7)Caution: Addition of excessive amounts of acid will interfere with the test procedures. The 2.0 ml of 25% H_2SO_4 per 500 ml sample should be added using a graduated or precise volume dispensing device. If no dispenser is available you may add exactly 40 drops of the 25% H_2SO_4. In most cases, the addition of 2.0 ml (40 drops) of 25% H_2SO_4 to 500 ml of surface water will reduce the pH to <2, however; if the pH remains above 2, add acid drop wise with stirring until the pH is lowered to <2. Although the requirement is for pH<2, the ideal range for Nutrients is a sample pH of 1.5-2.0. For most samples this pH can be achieved by adding 2.0ml of 25% H_2SO_4 per 500ml of water sample.
(8)In a glass container, submit a small quantity of the pure compound of any suspected material.
(9)Fill the bottle to overflowing and cap, leaving no air space.
(10)EPA Method 445.0, Revision 1.2, September 1997.
(11)Should only be used in the presence of residual chlorine. Add sodium thiosulfate or ascorbic acid (as specified) to the container first; fill at least half way before adding acid (if used). If residual chlorine is detected in a water sample (generally effluent), then it is recommended that the 500ml water sample for Nutrients be de-chlorinated at the time of sample collection. The recommended de-chlorination reagent for Nutrients is sodium thiosulfate (dissolve 3.5 grams in deionized water, then dilute to 1 liter). One mL of this solution will remove 1mg/L of residual chlorine in a 500 mL sample.
(12)Used by the DWR Chemistry Lab only at this time.
(13)The container types listed are those commonly used throughout the Division. Other container types may be acceptable. Please consult the laboratory about use of proper containers before deviating from those listed. (P-plastic, G-glass, P (disposable)-Plastic Disposable bottle)
(14)Samples submitted for purgeable halocarbons only should not be acid-preserved.
(15)Samples submitted for pesticide and acid herbicide analyses must be extracted within 72 hours of collection if the pH is not adjusted in the lab to a pH range of 5-9.
(16)Samples submitted for purgeable aromatics receiving no pH adjustment must be analyzed within 7 days of collection.
(17)The entire contents must be used for analysis.
(18) Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested on-site with lead acetate paper before pH adjustment in order to determine if sulfide is present. If it is, it can be removed by the addition of $CdNO_3$ powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to achieve a pH > 12.
(19) For dissolved metals, samples should be filtered with a 0.45micron filter immediately on-site before adding preservative.
(20) Sample preservation should be performed immediately upon collection. For composite 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 the samples may be preserved by maintaining at ≤ 6º C until compositing and sample splitting is completed.
(21) 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. Collection times must allow for sample preparation and analytical setup. Some samples may not be stable for the maximum time period given in the table. Collectors are obligated to hold the sample for as short a time as possible especially if knowledge exists showing that this is necessary to maintain sample stability.
(22) If the samples are oxidized (digested) with bromine chloride (BrCl) in the same bottle that they are collected, then the preservation of the sample may be delayed up to twenty-eight days after the time of sample collection. The total holding time with proper preservation for EPA Method 1631 is ninety days after collection. Reference: EPA Method 1631, Revision E, Section 8.5.
(23) Samples are cooled to 6° C at the time of collection. Due to the limitations of filtering samples in the field, it is the DWR Water Sciences Section's policy to filter chlorophyll *a* samples the day that the samples are received at the lab, not to exceed 24 hours from collection. Filters can be stored frozen in the dark for as long as 3 and 1/2 weeks without significant loss of chlorophyll a.

(24) Aqueous samples must be preserved ≤ 6º C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted a valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification "≤ ºC" is used in place of the "4 ºC" and "< 4 ºC" sample temperature requirements listed in some methods. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).
(25) Larger sample volumes may need to be submitted to achieve lower PQLs.
(26) If sample is not field preserved, HNO3 must be added 24 hours prior to analysis.
(27) The QAO has a licensed copy of ASTM D7365-09a, which details sampling, preservation and mitigating interferences in water samples for analysis of Cyanide. Special attention should be paid to the footnotes for any deviations.

Table 6.2. Required Containers, Preservation Techniques and Holding Times (Groundwater & Underground Storage Tank Sampling)

COLLECTION AND PRESERVATION OF GROUND WATER (including UST) SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Listed below is information to be used in the collection and preservation of ground water samples. Filtered samples are requested for some parameters as recommended by the USGS manual. **Excluding purgeable organics and sulfide**, a one-half inch air space should be left in all bottles to allow for mixing before analysis. **When submitting a filtered sample, write "DIS" (for dissolved) in the box beside the parameter(s) on the field sheet.**

NPDES, Appendix A, Federal Register, 38, No. 75, Pt II. NOTE: All other organics will be analyzed using methods from the Federal Register, 40 CFR Part 136 when available and Solid Waste 846 methods. The Branch Supervisor must approve methods from any other source.

Samples must be shipped to the Laboratory as soon as possible after collection. Reference: 40 CFR Part 136.3 Table II					
Parameter[2]	Minimum Required Volume	Container[1,14] P-Plastic G-Glass	(F) Filtered (U) Unfiltered	Preservation[18]	Maximum Holding Time[19]
Microbiology Parameters:					
Alkalinity[18] • includes bicarbonate & carbonate	200 ml	P (Disposable)	U	Cool ≤6°C[21]	14 days
BOD 5-day	1 liter	P	U	Cool ≤6°C[21]	48 hours[6]
CBOD 5-day	1 liter	P	U	Cool ≤6°C[21]	48 hours[6]
Coliform: Fecal, Total	250 ml (each)	P (sterile)[7]	U	Cool ≤6°C[21], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml) and 15% EDTA[7]	6 hours[8]
Specific Conductance	200 ml	P (Disposable)	U	Cool ≤6°C[21]	28 days
TOC	500 ml	P (Disposable)	U	H_3PO_4 to pH<2 Cool ≤6°C[21]	28 days
DOC	500 ml Include a Field Blank with DOC samples	P (Disposable)	F	Field filter using 0.45um pore size; H_3PO_4 to pH<2 Cool ≤6°C[21]	28 days

COLLECTION AND PRESERVATION OF GROUND WATER (including UST) SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Parameter[2]	Minimum Required Volume	Container[1,14] P – Plastic G – Glass	Filtered or Unfiltered	Preservation [18]	Maximum Holding Time[21]
Turbidity	200 ml	P (Disposable)	U	Cool ≤6°C[21]	48 hours[6]
Wet Chemistry Parameters:					
Bromide Chloride Fluoride Sulfate	500 ml	P (Disposable)	U	Cool ≤6°C[21]	28 Days
Color: Platinum Cobalt	400 ml	P (Disposable)	U	Cool ≤6°C[21]	48 hours[6]
COD	200 ml	P (Disposable)	U	25% H_2SO_4 to pH<2 Cool ≤6°C[21]	28 days
Cyanide, Total[23]	2 liters (2 x 1-liter bottles)	P	U	Add 0.6 g ascorbic acid[6], 6N NaOH to pH >10, not exceeding a pH of 11; Cool ≤6°C[24]	14 days[12]
Hexavalent Chromium	400 ml	P (Disposable)	U	Cool ≤6°C[21] pH 9.3-9.7	24 hours (notify lab of collection)
MBAS	500 ml	P (Disposable)	U	Cool ≤6°C[21]	48 hours[6] (notify lab of collection)
Oil & Grease	2 liters (2 x 1 liter-bottles)	G (wide-mouth quart jar, Teflon-lined cap)	U	1:1 H_2SO_4, pH<2 Cool ≤6°C[21]	28 days

COLLECTION AND PRESERVATION OF GROUND WATER (including UST) SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Parameter[2]	Minimum Required Volume	Container[1,14] P – Plastic G – Glass	Filtered or Unfiltered	Perservation[18]	Maximum Holding Time[19]
Phenols, Total Recoverable	2 liters (2 x 1-liter bottles)	G (Phenol bottle) only[5]	U	1:1 H_2SO_4 to pH<2 (1 ml Ferrous Ammonium Sulfate if sample contains oxidizer) Cool ≤6°C[21]	28 days
Residue, Suspended -Suspended Solids (plus Volatile/Fixed, if requested)	500 ml[22]	P (Disposable)	U	Cool ≤6°C[21]	7 days
Residue, Total -Total Solids (plus Volatile/Fixed, if requested)	500 ml[22]	P (Disposable)	U	Cool ≤6°C[21]	7 days
TDS -Total Dissolved Solids	500 ml[22]	P (Disposable)	U	Cool ≤6°C[21]	7 days
Silica	200 ml	P (Disposable)	U	Cool ≤6°C[21]	28 days
Sulfide	120 ml (40 ml x 3)[20]	G 40-ml VOA vial with Teflon-lined septum	U	Add 0.1 ml of 2N zinc acetate plus 6 N NaOH to pH>9. Cool ≤6°C[21] Leave no headspace in bottle.	7 days

COLLECTION AND PRESERVATION OF GROUND WATER (including UST) SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Parameter[2]	Minimum Required Volume	Container[1,14]	Filtered or Unfiltered	Preservation18	Maximum Holding Time[19]
Other Parameters					
Hardness, Total -request by checking Hardness, Total as CaCO3, or Ca and Mg, on field sheet. -or can be part of metals sample: Total Hardness=2.497[Ca mg/L]+4.118[Mg mg/L]	500 ml	P (Disposable)	U	1+1 HNO_3 to pH<2	6 months
pH	Inappropriate for laboratory analysis				Immediate - field measurement
Carbon Dioxide	Inappropriate for laboratory analysis				Immediate - field measurement
(Non-carbonate Hardness = total hardness- total alkalinity.) Non-carbonate Hardness [(3)]	Submit samples for total hardness (Ca+Mg) and alkalinity (as specified above)				
Nutrients Parameters:					
Ammonia (NH3-N)	500 ml (1 bottle for all, except when chlorine present; then include additional bottle of de-chlorinated sample for NH3-N)	P (Disposable)	U	25% H_2SO_4 to pH<2[9] Cool ≤6°C[21] 0.008% $Na_2S_2O_3$ to de-chlorinate (See note 11)	28 days
Nitrate-Nitrite (NO3+NO2 – N)					
Total Kjeldahl Nitrogen (TKN)					
Total Phosphorus (TP)					

COLLECTION AND PRESERVATION OF GROUND WATER (including UST) SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Parameter[2]	Minimum Required Volume	Container[1,14] P – Plastic G – Glass	Filtered or Unfiltered	Preservation[18]	Maximum Holding Time[19]
Dissolved Nutrients (4 parameters above)	200 ml (1 bottle)	P (Disposable)	F	Field filter using 0.45um pore size; 25% H_2SO_4 to pH<2[7]; Cool ≤6°C[24]	28 days
Nitrite (NO_2- N)	200 ml	P (Disposable)	U	Cool ≤6°C[21]	48 hours (notify lab of collection)
Nitrate (NO_3-N)	Calculated value using analytical results for NO3+NO2-N and NO2-N; submit samples for NO3+NO2-N and NO2-N				
Orthophosphate (PO_4-P)	200 ml	P (Disposable)	F	Filter immediately through 0.45-micron filter; Cool ≤6°C[21]	48 hours[6] (notify lab of collection)
Metals Parameters:					
Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn, and Hg[19]	500ml (1 bottle)	P (Disposable)	U	1+1 HNO_3 to pH<2, at least 24 hours prior to analysis	6 months (Hg 28 days)
Boron	500 ml	P (Disposable)	U	1+1 HNO_3 to pH<2	6 months
Mercury EPA 1631 E Hg (trace-level total Hg)	500 ml of sample; Plus a Field Blank must accompany each trace-level Hg sample	G(borosilicate), Teflon-lined cap	U	None required for total and dissolved Mercury – Use clean sampling techniques as described in EPA Method 1669.	28 days until preservation with BrCl[22] if the sample is oxidized in the sample bottle. Preserved samples are stable for up to 90 days from collection.

Organics Parameters: COLLECTION AND PRESERVATION OF GROUNDWATER (including UST) SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

Parameter[2]	Minimum Required Volume	Container[1,14] P – Plastic G – Glass	Filtered or Unfiltered	Preservation[18]	Maximum Holding Time[19]
Organics Parameters:					
Acid Herbicides	4 liters[10]	G (amber), Teflon-lined cap	U	Cool ≤6°C[21], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction[16], 40 days after extraction
Pesticides -Organochlorine -Organonitrogen -Organophosphorus	4 liters[10]	G (amber), Teflon-lined cap	U	Cool ≤6°C[21], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction[16], 40 days after extraction
Semi Volatile Organics (Base/Neutral & Acid Extractables)	4 liters[10]	G (amber), Teflon-lined cap	U	Cool ≤6°C[21], 0.008% $Na_2S_2O_3$ (0.1ml 10% $Na_2S_2O_3$ /125 ml)[11]	7 days until extraction 40 days after extraction
TPH Diesel Range (aqueous)	4 liters[10]	G (amber), Teflon-lined cap	U	Cool ≤6°C[21]	14 days; analyze extract within 40 days
Volatile Organics (VOA)	40 ml x 4[20] A Trip Blank (3 vials) must accompany all VOA samples.	G, VOA vials Teflon-lined septum	U	Cool ≤6°C[21], 0.6g ascorbic acid only if residual chlorine present, Sodium Bisulfate ($NaHSO_4$)[13] to pH 2 [15,17]. Leave no headspace in bottle.	14 days (7 days for aromatics only when unpreserved)
TPH Gasoline Range (aqueous)	40 ml x 4[20]. A Trip blank (3vials) must accompany all VOA samples	G, VOA vials Teflon-lined septum	U	Cool ≤6°C[21], 0.6g ascorbic acid only if residual chlorine present, Sodium Bisulfate ($NaHSO_4$)[13] to pH<2 [15,17]. Leave no headspace in bottle.	14 days

COLLECTION AND PRESERVATION OF GROUND WATER (including UST) SAMPLES FOR THE NC DWR WATER SCIENCES SECTION

SOIL & SEDIMENT SAMPLES

**WHEN SUBMITTING SOIL AND SEDIMENT SAMPLES FOR ANALYSIS, A SEPARATE SAMPLE CONTAINER MUST BE COLLECTED FOR EACH OF THE ANALYTICAL GROUPS LISTED BELOW:

Parameter	Minimum Required Volume	Container[14,1] P-Plastic G-Glass	Preservation[18]	Maximum Holding Time [19]
Oil and Grease	8 oz jar	G, Teflon-lined cap	Cool ≤6°C, 1ml concentrated HCl per 100 grams soil to pH < 2	28 Days
Metals : Ag , Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sn, Se, Tl, V, Zn and Hg	8 oz jar	G, Teflon-lined cap	Cool ≤6°C	6 Months (Hg 28 days)
Pesticides/PCB's (OC/ON/OP)	8 oz jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; analyze w/in 40 days
Acid Herbicides	8 oz jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; analyze w/in 40 days
Semi Volatile Organics (BNAs)	8 oz jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; analyze w/in 40 days
Volatile Organics (VOA)	4 oz jar + trip blank	G, Teflon-lined cap or septum	Cool ≤6°C	14 days
TPH Gas Range (soil)	4 oz jar + trip blank	G, Teflon-lined cap or septum	Cool ≤6°C	14 days
TPH Diesel Range (soil)	8 oz jar	G, Teflon-lined cap	Cool ≤6°C	14 days to extract; Analyze w/in 40 days

(1)P-Plastic, G- Glass, P(Disposable) - Plastic disposable bottle.
(2)Parameters grouped together e.g. Nutrients, may be submitted in the same bottle.
(3)When non-carbonate hardness is requested, samples for both metals (Ca+Mg) and alkalinity must be submitted.
(4)Add 0.6 g of ascorbic acid only if sample contains residual chlorine.
(5)Use one liter round glass bottles labeled phenol.
(6)48 hours is the maximum holding time; however, samples should be submitted to lab as soon as possible.
(7)Use the 250 ml wide-mouth sterile plastic bottles for all samples. All bottles contain sodium thiosulfate and EDTA reagents. Do not rinse.
(8)Litigation samples must be delivered to the laboratory within 6 hours of sample collection to meet 8 hour hold time.

(9) Caution: Addition of excessive amounts of acid will interfere with the test procedures. The 2.0 ml of 25% H_2SO_4 per 500 ml sample should be added using a graduated or precise volume dispensing device. If no dispenser is available, you may add exactly 40 drops of the 25% H_2SO_4. In most cases, the addition of 2.0 ml (~40 drops) of 25% H_2SO_4 to 500 ml of groundwater will reduce the pH to <2; however, if the pH remains above 2, add acid dropwise with stirring until the pH is lowered to <2. For nutrient samples, the pH range of 1.5-2.0 is ideal to insure best possible recovery of analytes. Although the requirement is for pH<2, the ideal range for Nutrients is a sample pH of 1.5-2.0. For most samples this pH can be achieved by adding 2.0ml of 25% H_2SO_4 per 500ml of water sample.
(10)In a glass container, submit a small quantity of the pure compound of any suspected material.
(11Should only be used in the presence of residual chlorine. Add sodium thiosulfate or ascorbic acid (as specified) to the container first; fill at least half way before adding acid (if used). If residual chlorine is detected in a water sample (generally effluent), then it is recommended that the 500ml water sample for Nutrients be dechlorinated at the time of sample collection. The recommended de-chlorination reagent is sodium thiosulfate (dissolve 3.5 grams in deionized water, then dilute to 1 liter). One mL of this solution will remove 1mg/L of residual chlorine in a 500 mL sample.
(12)Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested on-site with lead acetate paper before pH adjustment 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.
(13)Used by the DWR Chemistry Lab only at this time.
(14)The container types listed are those commonly used throughout the Division. Other container types may be acceptable. Please consult the laboratory about use of proper containers before deviating from those listed above.
(15)Samples submitted for purgeable halocarbons only should not be acid-preserved.
(16)Samples submitted for pesticide and acid herbicide analyses must be extracted within 72 hours of collection if the pH is not adjusted in the lab to a pH range of 5-9.
(17)Samples submitted for purgeable aromatics receiving no pH adjustment must be analyzed within 7 days of collection.
(18) Sample preservation should be performed immediately upon collection. For composite sample, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then the samples may be preserved by maintaining at 6ºC until compositing and sample splitting is completed.
(19) 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. Collection times must allow for sample preparation and analytical setup. Some samples may not be stable for the maximum time period given in the table. Collectors are obligated to hold the sample for as short a time as possible especially if knowledge exists showing that this is necessary to maintain sample stability.
(20) Fill the bottle to overflowing and cap, leaving no air space.
(21) Aqueous samples must be preserved ≤ 6º C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted a valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification "≤ ºC" is used in place of the "4 ºC" and "< 4 ºC" sample temperature requirements listed in some methods. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).
(22) Larger sample volumes may need to be submitted to achieve lower PQLs.
(23) The QAO has a licensed copy of ASTM D7365-09a, which details sampling, preservation and mitigating interferences in water samples for analysis of Cyanide. Special attention should be paid to the footnotes for any deviations.

7.0 Sample Custody and Handling

Many of the inaccuracies in environmental analysis result from incorrect sample handling and lack of supporting documentation. Four factors that may ultimately affect the integrity of reported data include 1) obtaining a representative sample, 2) preventing contamination of the sample, 3) providing legal documentation of the sampling event, and 4) protecting the sample from chemical, physical or biological change prior to analysis.

7.1 Objective

The primary objective of sample custody is to maintain the integrity of samples and to generate documentation sufficient to trace a sample from its point of origin, through receipt in the laboratory, then analysis, reporting and disposal.

While the laboratory may not have control of field sampling activities, the laboratory has incorporated the following into its Quality Management Plan to ensure the validity of the laboratory's data.

- The laboratory has established guidelines and procedures for the transportation, receipt, handling, protection, storage, retention or disposal of samples including all provisions necessary to protect the integrity of the sample and to protect the interests of the laboratory and the client. These procedures are communicated to Water Sciences Section personnel and its clients in the *Sample Submission Guidance* document. This document is available for viewing on the Water Sciences Section website at: http://portal.ncdenr.org/web/wq/lab/ops/samples
- The laboratory has adopted a system for identifying and tracking samples. This identification is retained throughout the life of the sample in the laboratory and ensures that samples cannot be confused physically or when referred to in records or other documents.

The sample management procedures used by the DWR Water Sciences Section Chemistry Laboratories are designed to ensure that sample integrity is maintained and documented. This documentation includes:

- Sample transmittal forms (fieldsheets and Chain-of-Custody)
- Sample preparation logs or worksheets
- Sample analysis logs or worksheets
- Calibration and quality control data associated with a sample set
- Instrument maintenance logs
- Sample disposal logs
- Final reports

7.2. Sample Custody Procedures

The Water Sciences Section follows both routine and legal chain-of-custody (COC) procedures, depending on the requirements of the client submitting the samples. The DWR Water Sciences Section has adopted a policy of maintaining formal COC records on samples collected during enforcement or other investigations suspected to involve litigation. All samples processed by the Water Sciences Section Chemistry Laboratory are kept discrete by assigning an individual laboratory number.

7.2.1. Routine Sample Custody

Samples are collected by field personnel utilizing procedures identified within their field SOPs or Quality Assurance Plans. The sample collection personnel must first consider the analyses to be performed so that proper shipping containers and sample containers with the appropriate preservatives are assembled. Holding times and field quality control measures must also be considered. All records required for documentation of field collection, including the pertinent data on sample labels/tags and applicable fieldsheets must be completed by the field personnel. Samples are packed so that they are segregated by site, sampling location, sample analysis type or by sample priority.

A sample transmittal form (fieldsheet) must accompany all samples that are submitted to the Water Sciences Section. This record serves as a documented summary of the sample collection event and includes all records necessary to trace a sample from its point of origin through the final report. Each event or procedure to which

the sample is subjected is recorded including sample collection, field preservation, sample receipt and sample log in. Example fieldsheet supplied by the Central Laboratory are shown in Figures 7.1 through 7.4 covering submissions to the Central Laboratory, Asheville Laboratory, Underground Storage Tank sampling, and Sediment, Soil & Tissue sampling. The minimum information required on these records includes:

(a) a unique sample location/field ID combination for that date/time/collector.
(b) the date and time of sample collection (beginning and ending for composite samples)
(c) the collector's name
(d) the submitting entity (who to report to)
(e) the sample matrix
(f) the analyses requested
(g) sample priority
(h) method of shipment

If any of the above information is not present, an effort is made to reach the collector by phone. If the information cannot be obtained in a timely manner, the sample is subject to rejection. After collection, the samples are shipped to the laboratory by state courier, common carrier or are hand-delivered by the field staff.

Additional documentation recorded on the field sheets may include:

- Ambient field conditions
- Type of composite
- Temperature of samples in the field
- Field measurement data
- Field instrument calibration information

7.2.2. Legal Chain of Custody

Legal chain of custody is a special type of sample custody in which documentation is kept of all events (i.e., possession, transport, storage, and disposal) and time intervals associated with a specific sample. Legal chain of custody documentation includes chain-of-custody (COC) forms that have adequate space for dated, original signatures of all individuals who handled the samples, from the time of collection through laboratory receipt and distribution to the analytical unit. The custody of a sample is defined as one of the following:

(a) It is in the sampler's or transferee's actual possession;
(b) It is in the sampler's or transferee's view, after being in his/her physical possession;
(c) It was in the sampler's or transferee's physical possession and then he/she secured it or placed in a designated secure area to prevent tampering.

The purpose of the COC is to supply a detailed record of the sample description, collection information, and any transfer of custody from sample collection through sample receipt into the laboratory. The sample collector is responsible for the care, custody and paper trail documentation of the sample until properly dispatched to the analytical laboratory via State courier or turned over to a sample custodian or designee. The sample collector must assure that each container is in his/her physical possession or in his/her view at all times, or stored in such a place and manner to preclude tampering. Samples must be delivered to the laboratory as soon as possible after collection.

NOTE: The State couriers and independent couriers are not required to sign the COC form. The samples and COC are kept in the sealed sample cooler with the associated samples. The condition of the security seal is noted upon receipt at the lab. The freight bill from independent couriers is kept with the chain-of-custody documentation.

Chain of custody records shall include the following information either by direct entry or by linkage to the fieldsheet:

- Time of day and calendar date of each transfer or handling procedure
- Signatures of transferors and transferees
- Location and security conditions of samples (when stored in the field)
- Storage conditions for sample including thermal preservation
- Unique lab ID for all samples
- Common carrier documents
- Sampling site description
- Date and time of sample collection
- Unique field ID code (optional)
- Collector's name
- Number of sample containers
- Requested analyses

Entries into all records must be written legibly and must be made with waterproof ink. All documentation entries shall be signed or initialed by responsible staff. Erasures or markings shall not obliterate entries in records. All corrections to record-keeping shall be made by one line marked through the error leaving the original record visible. The individual making the correction shall sign or initial and date the correction.

An example COC form is given in Figure 7.5 (Water Quality Section Surface Water Chain of Custody Form). A copy of this record is sent to the customer while the original is kept in the sample report file.

7.3 Sample Receipt Protocol

Sample acceptance, receipt, tracking and storage procedures are fully detailed in sample management SOPs. These procedures are summarized in the following sections.

The chemists at the Regional Laboratory and the Support Unit personnel at the Central Laboratory are responsible for receiving samples shipped or delivered by field personnel that collect water, soil or tissue samples throughout the state. Laboratory staffs receive deliveries of all samples and initiate the first in-house records for a sample. When samples arrive at the laboratory, laboratory personnel inspect the coolers and samples. The integrity of each sample must be determined by comparing sample labels or tags with the fieldsheet and COC (when applicable) and by visual checks of the container for possible damage or tampering. Any problems or anomalies are recorded on a Sample Condition Upon Receipt (SCUR) form and the sampler is notified. A course of action is determined and documented and the SCUR form is scanned into Laserfiche and the shared drive Chem Lab folder along with the fieldsheets in the Fieldsheets folder. Copies of the SCURs are scanned and stored on the server at S:\ChemLab\Fieldsheets and also in Laserfiche. A copy of the SCUR is filed with the printed final report. A copy of this form is sent with the final report to the collector.

7.3.1 Procedure

Laboratory staffs remove the samples from the container or cooler and organize the sample bottles according to sample location and fieldsheet. A sample may be composed of greater than one bottle since different preservatives, collection or handling techniques may be required to perform all analyses requested. (Sample integrity and condition of all sample containers is verified for leakage, broken bottles, contaminated coolers, odors, etc.)

Inspection of samples, at the time of receipt, includes checking:

(a) Complete documentation to include sample identification, location, date and time of collection, collector's name, preservation type, sample type and any additional comments concerning the samples.

(b) Complete sample labels to include unique identification, preservation, analysis requested, date and time of collection and collector in indelible ink.

(c) Use of appropriate sample containers.

(d) Adherence to holding times as specified in the test method or summarized in Section 6.

(e) Adequate sample volume for the required analyses.

(f) Damage or signs of contamination to the sample container. Volatile organics vials and other highly volatile samples (e.g., sulfide) are also inspected for headspace.

(g) Checking and recording the temperature of samples that require thermal preservation.

Verification of chemical sample preservation, as specified in 40 CFR Part 136 or the test method, is performed immediately upon receipt in the analytical units after login and distribution and the process is documented on appropriate logs or bench sheets. Exceptions include volatile organics, sulfide and coliform samples. The preservations of these samples are checked after an aliquot is taken for analysis in order to avoid volatilization or contamination. Wide range and narrow-range pH test strips are used to verify chemical preservation. If anomalies are noted or if adjustments have to be made, the process is documented on a Sample Anomaly Report (SAR) and the sample results are qualified accordingly. When the pH of a sample is adjusted in the laboratory, the observed and adjusted pHs must be recorded as well as the amount of acid or base the was used to make the adjustment. When an analyst is unable to confirm proper preservation using the test strips, a pH meter and electrode shall be used to document an actual pH value for the sample. Otherwise, the pH may be documented as "less than" or "greater than" the published criteria (for example, *<2* or *>10*).

At the time of receipt, laboratory staff checks the temperature of the samples by measuring the temperature of the temperature blank using an IR gun thermometer. The IR gun thermometers are checked daily against a calibrated thermometer and the results documented on the IR Daily Calibration Check log. The IR thermometer must be within +/- 1 degree C of the calibrated thermometer. Corrective action must be taken if the temperatures differ by greater than 1 degree C. The IR thermometers are checked annually against a blackbody reference standard.

If there is no temperature blank present and if it does not compromise the integrity of the sample, the temperature of a representative sample is measured by pouring a small aliquot into a separate container, taking the temperature of this portion and then discarding it or checking temperature with the calibrated IR thermometer. Samples shall be deemed acceptable if arrival temperature is either within 0.1 to 6°C (with no evidence of freezing), 0.1 to <10°C for bacteriologicals or the method specific range. Samples that are hand-delivered immediately after collection may not be at the required temperatures; however, if there is evidence that the chilling process has begun, such as the arrival on ice or ice slurry and a downward trend in temperature is documented, the sample shall be considered acceptable. For samples with short transport times, samplers are asked to document a field temperature. Documentation of the actual sample temperature at the time of collection and upon receipt (and demonstrating a downward trend) will complete the preservation documentation requirements.

For COC samples, shipping documents are set aside and the shipping container examined, noting the presence and condition of any custody seals on the outside of the container before the sample is accepted for analysis. Any internal custody seals are then examined. Observations are recorded in the space provided on the COC form. The shipping container is opened fully and the sample custody documentation removed. If there is no COC or if it is improperly filled out, the deviation is documented on a SCUR form and chain of custody procedures areconsent generally discontinued at this point. Carrier, freight bill or other tracking numbers in shipping documentation are recorded on or retained with the COC.

Any deviations from the checks above that question the suitability of the sample for analysis, or incomplete documentation of the tests required will be resolved by consultation with the sampler. If the sample acceptance criteria are not met, the laboratory will:

1. Notify the customer of any non-conformance that may affect the integrity of the data. The samples may be rejected unless the client requests otherwise. Data from compromised samples is flagged with the appropriate data qualifier code(s) or comments and Sample Anomaly Report is issued with the report.

2. Fully document any decision to proceed with sample analysis that does not meet sample acceptance criteria. The condition of these samples shall be documented on the SCUR. The analytical results shall be appropriately qualified on the final report.
3. Retain all correspondence or records of communications with the sampler regarding the disposition of rejected samples.

The custodian then assigns a chronological lab number thru LIMS entry to each sample and records their initials, shipment method and the date and time of receipt. The lab number is recorded on each sample label or tag and on the COC form when applicable. Each sample is assigned a unique sample identification number of the format XXWYYYY or XXGYYYY where X is the number denoting the year, then either W (representing Water Quality Surface Water) ,G (representing Water Quality Ground Water) or U (representing Underground Storage Tank, UST) represents the type of sample and YYYY is an accession number beginning with '0001'.

If samples are identified for legal/evidentiary purposes on the fieldsheet, laboratory staffs will retain the shipping record with the COC, initiate an internal COC for laboratory use by analysts and a sample disposal record. When a sample is removed from the Receiving Room, the custody is transferred from the sample custodian to an analyst. This person may be one and the same at the regional laboratories. The transaction is recorded in the "lab use only" section of the COC form by date, time and user.

Samples designated as 'Emergency' receive priority handling. Colored stickers denote their priority status for quick identification and all other work or sample analyses are often preempted by these samples. Appendix V of this document states WSS Laboratory Sample Prioritization Policy.

Copies of the fieldsheets are scanned and stored on the server at S:\ChemLab\Fieldsheets and also in Laserfiche®. The originals are sent to a Processing Assistant for entry into the laboratory data management system. All samples received by the Water Sciences Section are assigned an AD, AE etc. number and logged into the LABWORKS™ LIMS. The samples are logged into the LABWORKS™ LIMS with the following information.

(a) lab number (ADxxxxx,AExxxxx etc)
(b) sample location/id/description
(c) county
(d) sorting number
(e) station number (as appropriate)
(f) location code
(g) the program or region to report the data to
(h) sample collector
(i) date and time collected
(j) date and time received
(k) sample type
(l) sample priority
(m) analyses requested
(n) initials of the sample receipt person
(o) person releasing the report
(p) date report released

This information must be unequivocally linked to the sample record or included as part of the record. If such information is recorded or documented elsewhere, the records shall be part of the lab's permanent records, easily retrievable upon request and readily available to individuals who will process the sample. Note: Information placed or recorded on the sample container or tag is not considered permanent record.

All log-in information is cross-checked by a second Processing Assistant, after which login of the sample is authorized in the LABWORKS™ LIMS. The fieldsheets are placed in a notebook or central location to await final report generation.

7.4 Procedure to Assess Capability to Meet Workload Requirements

It is the primary responsibility of the Section Chief, through the Environmental Program Supervisors, Supervisors and Lead Chemists, to manage workload in the lab. Availability of capability in the lab is contingent on both labor and instrumentation. All samples are logged into the LABWORKS™ LIMS and given a unique lab number (AD) as well as an ID number associating the sample with Water Quality Program Surface Water (WQ), and Groundwater (GW) as well as UST (U). It is the responsibility of the Lead Chemist for each analytical unit to review the incomplete work list daily with the chemists/technicians and report any problems with scheduling to the Environmental Program Supervisor. The Environmental Program Supervisor maintains a detailed status report, which provides information on all samples that are logged into the lab. This information includes due date and incomplete summary. Scheduling and instrument issues on a unit by unit basis are discussed and resolved. The Lead Chemists track analytical units with limited capacity or scheduling issues and passes this information to the Environmental Program Supervisor to notify samplers.

Sample collection dates/times are entered during sample login. The holding time deadline is calculated from this information and noted on the backlog report. For a grab sample, the holding time begins at the time of collection. For a composite sample collected automatically over time (e.g., using a 24-hour composite sampler) the holding time begins at the time of the end of collection of the composite samples. Environmental Program Supervisors have the responsibility to ensure all analyses under their supervision are prepared and analyzed within the holding times. Chemists and technicians who schedule their work priority from backlog reports have the responsibility to complete analytical work within the holding time.

7.5 Storage conditions

After receipt and check-in, samples are transferred from the sample receiving area to the analytical units or sample storage areas. Storage areas must not contribute to deterioration, contamination, loss or damage to the sample. When samples must be stored under specified environmental conditions, these conditions shall be maintained monitored and recorded. The primary considerations for sample storage are temperature, holding times, contamination and security.

Samples are stored in the following areas within the Central Laboratory:

(a) air conditioned room (G-113): aqueous metal samples
(b) walk-in refrigerator (G035A): organic samples (SVOA, pesticides)
(c) walk-in refrigerator (G028): nutrients and wet chemistry samples
(d) walk-in refrigerator (G088): sediment metal and microbiology samples
(e) VOA lab refrigerator #1 (G065): VOA sample secondary aliquots
(f) VOA lab refrigerator #2 (G065): aqueous and sediment VOA samples
(g) lab freezer (G113): tissues and other samples requiring freezing
(h) lab freezer (G066): filtered chlorophyll *a* samples
(i) lab freezer (G035A): Pesticide tissue samples

The regional laboratory stores samples in refrigerators located in the analytical areas.

Section 6.0 summarizes the temperature and holding time protocols for various analyses. Samples, sample fractions, extracts, digestates or other sample preparation products that require thermal preservation shall be kept at +/- 2°C of the test method requirements. Those samples that have a specified storage temperature of 6°C may be stored at 0.1 to 6°C as long as there is no evidence of freezing. The temperature of cold storage areas are monitored and recorded daily and corrective action is taken as necessary.

All samples distributed into the laboratory are stored separately from standards and reagents used for analyses to prevent cross-contamination. Samples are also stored away from food and other potentially contaminating sources. Sample fractions, extracts, digestates, and other sample preparation products are stored according to Section 6.0 (or according to the specifications in the test method) in controlled storage areas in the analytical unit.

The Water Sciences Section laboratories are limited access, secure facilities. Only authorized personnel are permitted within the laboratory areas where sample access is possible. Access to the laboratory is controlled such that sample storage need not be locked at all times unless a particular case demands it. Samples are accessible to DWR Water Sciences Section Laboratory personnel only. Visitors to the laboratory are prohibited from entering the refrigerator and laboratory areas unless

accompanied by an employee of the Water Sciences Section. Samples are returned to the appropriate refrigerator after sufficient sample has been obtained to complete the analysis.

7.6 Sample Disposal

Samples are normally maintained in the lab no longer than three months from receipt unless otherwise requested. If the sample is part of litigation, the affected legal authority, data user, or sample submitter must participate in the decision about the sample's disposal.

Disposal is performed in accordance with local, state, US EPA-approved methods and in accordance with the Laboratory Chemical Hygiene Plans. All documentation and correspondence concerning the disposal decision process must be kept on file. Pertinent information includes:

- Date of disposal
- Nature of disposal (e.g., sample depletion)
- Names of individuals who conducted arrangements and physically completed the task.

Sample disposal may be handled in the following manner:

1) The sample may be consumed completely during analysis, or
2) If samples meet established disposal guidelines, they are discarded by pouring down sink drains. The laboratory's sanitary sewer system is equipped with a limestone pit for normalizing pH.

7.7 Sample Custodians

Personnel working in the sample receiving room or sample receiving area are designated as sample custodians. The supervisors, chemists, technicians and QA/QC Coordinator may also be designated as sample custodians.

7.8 Inter-laboratory Custody

Samples that need to be subcontracted or routed to another laboratory within the Water Sciences Section will show transfer to that lab on a sample transmittal form, which lists sample ID numbers and requested analyses. It will include the date/time it was sent out and the identity of the custodian responsible. For chain of custody samples, the COC form is completed and scanned onto S:\ChemLab\Fieldsheets and Laserfiche with the associated samples for review. The delivery technician and the recipient at the receiving lab must sign the COC indicating the transfer dates and times.

7.9 DWR LABWORKS™ LIMS

The laboratory uses **LABWORKS™ LIMS**. The main server, the applications and hardware are maintained by NC IT. LABWORKS™ is a commercial LIMS product purchased from Perkin Elmer (the server is maintained at Street, Raleigh, NC 27603).

To gain access to Labworks™ LIMS, users must provide valid network and LIMS usernames and passwords.

When all the analyses for a sample are complete, data generated is entered into **LABWORKS™ LIMS**, peer reviewed and senior reviewed the sample is authorized for released. The Supervisors or the Section Chief certifies the reports by initialing them. One report is retained with the field data sheets in the laboratory. The other report is mailed with a copy of the fieldsheet to certain clients. Other clients access the report via **LABWORKS™ LIMS**.

The LIMS software is being modified on a continuing basis by the section. The revisions of the codes are documented in the project history file of each application. The verification of the performance of the LIMS software or hardware is performed each time when any part of it is used. Any abnormalities are reported to the Microbiology and Inorganic Chemistry Branch Supervisor or Wet Chemistry/ Nutrients Unit Supervisor immediately for quick corrective action(s).

Figure 7.1. NC DWR Central Laboratory (WSS) Field Sheet.

North Carolina Division of Water Resources
Central Laboratory (Water Sciences Section)

Water Sample Collection & Submittal Form

Visit ID: (optional) | Tag ID

Lab Use Only:
Laboratory Sample Number:
Date Received:
Time Received:
Received By:
Delivery Method: ☐ State Courier ☐ Hand Delivery ☐ Other:
Temperature (°C) on Arrival:

Location Description:
Location Code:
County:
Collector:
DWR Region: (based on county)
DWR Office: (or agency name)
River Basin:
Date:
Notes:
Time:
☐ Chlorinated ☐ De-chlorinated in Field
Sampling Method: ☐ Grab ☐ Composite ☐ Other:
☐ Filtered in Field — Dissolved analysis: Enter "DIS" in check-boxes for parameters
Sample Depth:

Priority: ☐ Ambient ☐ Routine ☐ Compliance ☐ COC ☐ Emergency ☐ QA
Water Matrix: ☐ Surface ☐ Ground ☐ Waste ☐ Blank ☐ Solution
Location Type: ☐ River/Stream ☐ Lake ☐ Estuary ☐ Canal ☐ Stormwater ☐ Monitoring Well ☐ Water Supply ☐ Effluent ☐ Influent ☐ Field Blank ☐ Trip Blank ☐ Filter Blank ☐ Other:

Collector's Comments:

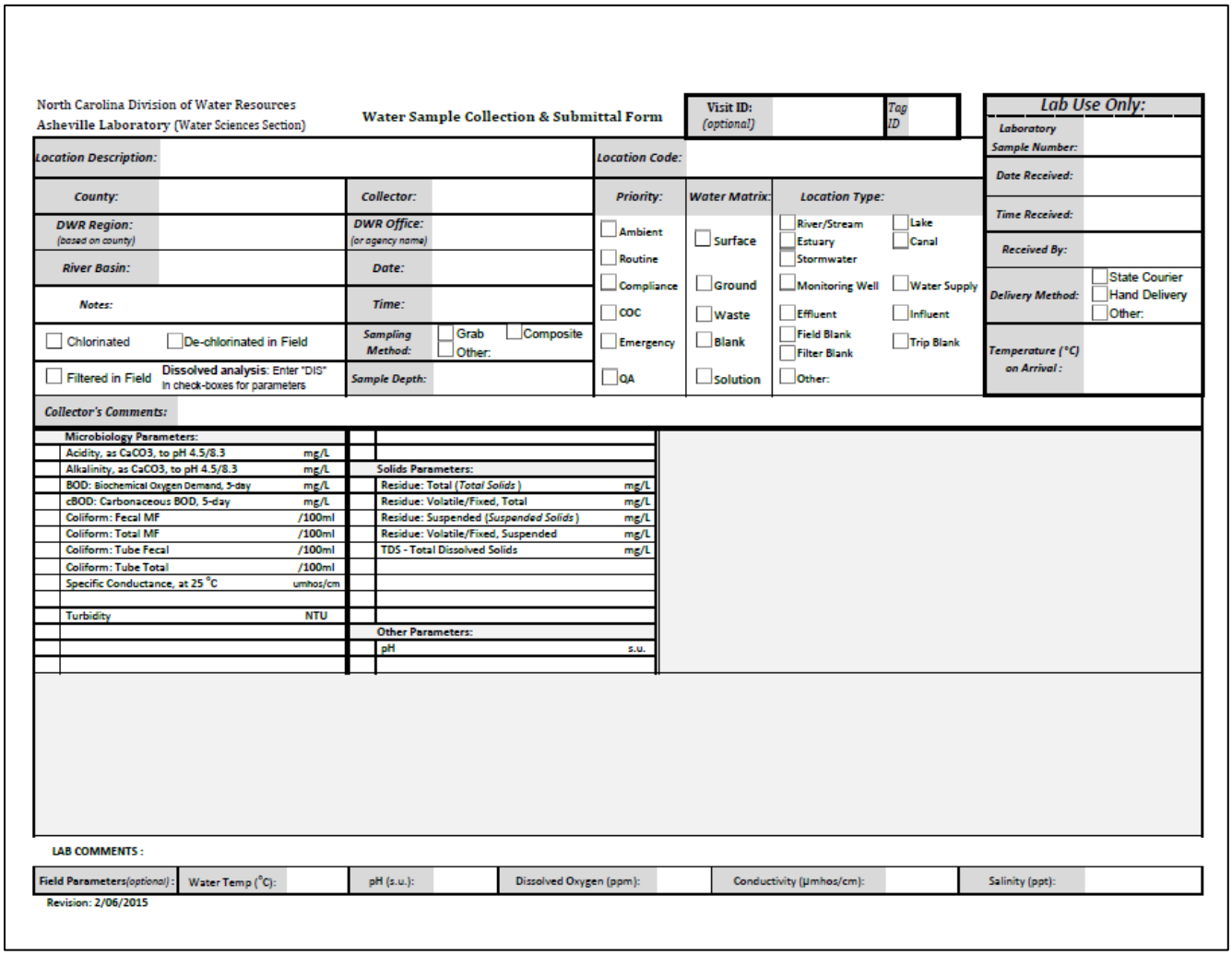
Microbiology Parameters:		MBAS (surfactants)	mg/L	Metals Parameters:		Tin (Sn)	µg/L
Acidity, as CaCO3, to pH 4.5/8.3	mg/L	Oil and Grease, HEM, Total Recoverable	mg/L	Aluminum (Al)	µg/L	Titanium (Ti)	µg/L
Alkalinity, as CaCO3, to pH 4.5/8.3	mg/L	Phenols, Total Recoverable	µg/L	Antimony (Sb)	µg/L	Vanadium (V)	µg/L
BOD: Biochemical Oxygen Demand, 5-day	mg/L	Residue: Total (*Total Solids*)	mg/L	Arsenic (As)	µg/L	Zinc (Zn)	µg/L
cBOD: Carbonaceous BOD, 5-day	mg/L	Residue: Volatile/Fixed, Total	mg/L	Barium (Ba)	µg/L		
Coliform: Fecal MF	/100ml	Residue: Suspended (*Suspended Solids*)	mg/L	Beryllium (Be)	µg/L	Boron (B), Total	µg/L
Coliform: Total MF	/100ml	Residue: Volatile/Fixed, Suspended	mg/L	Cadmium (Cd)	µg/L	Mercury 1631, low-level	ng/L
Coliform: Tube Fecal	/100ml	TDS - Total Dissolved Solids	mg/L	Calcium (Ca)	mg/L		
Coliform: Tube Total	/100ml	Silica	mg/L	Chromium (Cr), Total	µg/L	Organics Parameters:	
Specific Conductance, at 25 °C	umhos/cm	Sulfide	mg/L	Cobalt (Co)	µg/L	Acid Herbicides	
TOC - Total Organic Carbon	mg/L	Tannin & Lignin	mg/L	Copper (Cu)	µg/L	Organochlorine Pesticides	
Turbidity	NTU			Iron (Fe)	µg/L	Organonitrogen Pesticides	
		Other Parameters:		Lead (Pb)	µg/L	Organophosphorus Pesticides	
Wet Chemistry Parameters:		pH	s.u.	Lithium (Li)	µg/L	PCBs (polychlorinated biphenyls)	
Bromide	mg/L	Hardness, Total as CaCO3 - by titration	mg/L	Magnesium (Mg)	mg/L		
Chloride	mg/L			Manganese (Mn)	µg/L	Semi-Volatile Organics (BNAs)	
Fluoride	mg/L			Mercury (Hg)	µg/L	TPH Diesel Range	
Sulfate	mg/L	Nutrients Parameters:		Molybdenum (Mo)	µg/L		
Chlorophyll a	µg/L	Ammonia as N (NH3-N)	mg/L	Nickel (Ni)	µg/L	Volatile Organics (VOA)	
Color: ADMI	c.u.	Nitrate-Nitrite as N (NO3+NO2-N)	mg/L	Potassium (K)	mg/L	MTBE/BTEX	
Color: Platinum Cobalt	c.u.	Total Kjeldahl Nitrogen as N (TKN)	mg/L	Selenium (Se)	µg/L	TPH Gasoline Range	
COD: Chemical Oxygen Demand	mg/L	Total Phosphorus as P (TP)	mg/L	Silver (Ag)	µg/L		
Cyanide, Total	mg/L	Nitrite as N (NO2-N)	mg/L	Sodium (Na)	mg/L	Biological:	
Formaldehyde	mg/L	Nitrate as N (NO3-N calculated)	mg/L	Strontium (Sr)	µg/L	Phytoplankton / Algae	
Hexavalent Chromium (Cr6+)	mg/L	Orthophosphate as P (PO4)	mg/L	Thallium (Tl)	µg/L		

LAB COMMENTS :

Field Parameters(optional):	Water Temp (°C):	pH (s.u.):	Dissolved Oxygen (ppm):	Conductivity (µmhos/cm):	Salinity (ppt):

Revision: 2/06/2015

Figure 7.2. NC DWR (WSS) Asheville Regional Office Laboratory Field Sheet.



North Carolina Division of Water Resources
Asheville Laboratory (Water Sciences Section)

Water Sample Collection & Submittal Form

Visit ID: (optional) | Tag ID

Lab Use Only:
Laboratory Sample Number:
Date Received:
Time Received:
Received By:
Delivery Method: ☐ State Courier ☐ Hand Delivery ☐ Other:
Temperature (°C) on Arrival:

Location Description:
Location Code:

County:
Collector:
DWR Region: (based on county)
DWR Office: (or agency name)
River Basin:
Date:
Notes:
Time:
☐ Chlorinated ☐ De-chlorinated in Field
Sampling Method: ☐ Grab ☐ Composite ☐ Other:
☐ Filtered in Field — Dissolved analysis: Enter "DIS" in check-boxes for parameters
Sample Depth:

Priority: ☐ Ambient ☐ Routine ☐ Compliance ☐ COC ☐ Emergency ☐ QA
Water Matrix: ☐ Surface ☐ Ground ☐ Waste ☐ Blank ☐ Solution
Location Type: ☐ River/Stream ☐ Lake ☐ Estuary ☐ Canal ☐ Stormwater ☐ Monitoring Well ☐ Water Supply ☐ Effluent ☐ Influent ☐ Field Blank ☐ Trip Blank ☐ Filter Blank ☐ Other:

Collector's Comments:

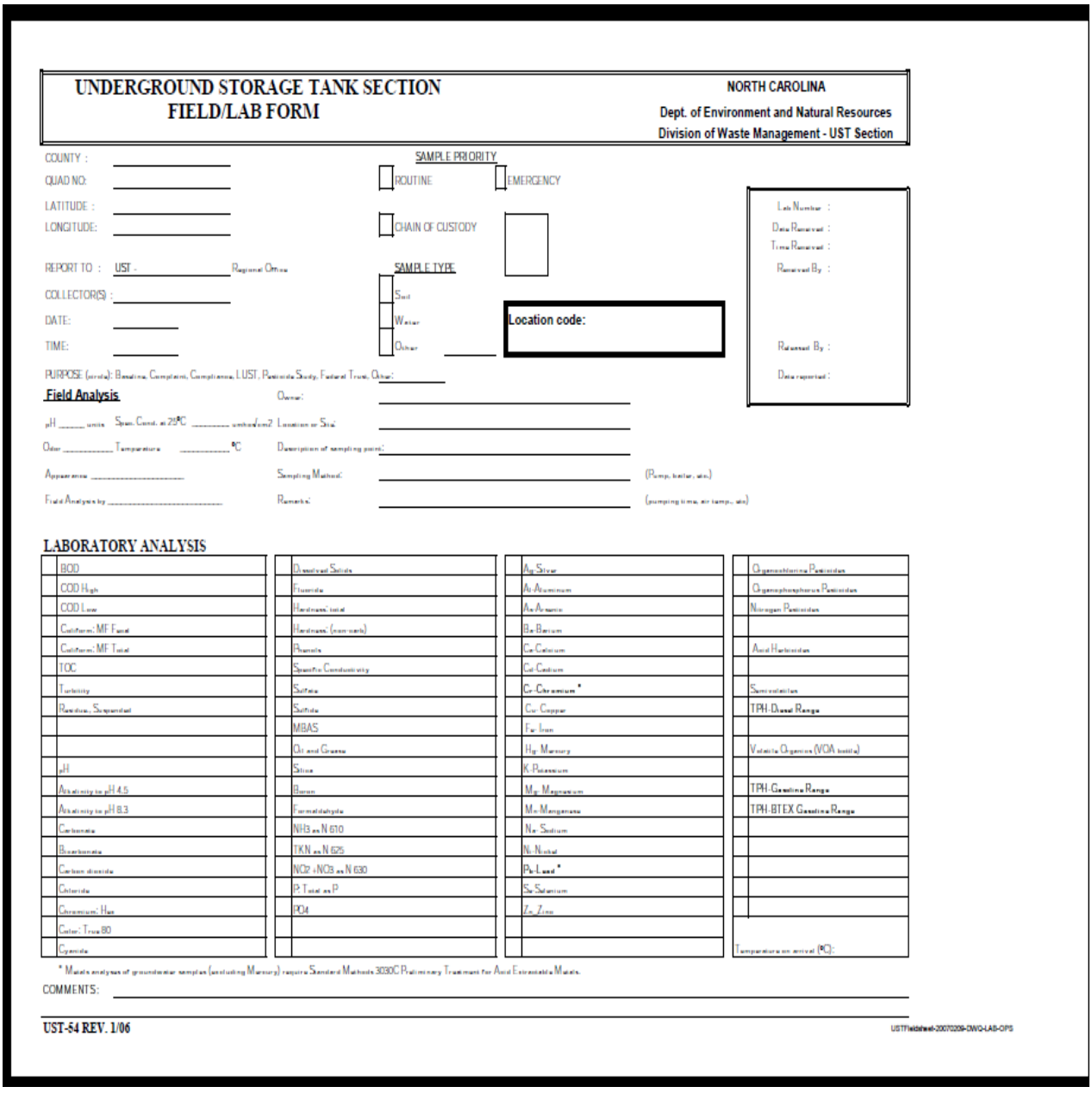
Microbiology Parameters:		Solids Parameters:	
Acidity, as CaCO3, to pH 4.5/8.3	mg/L		
Alkalinity, as CaCO3, to pH 4.5/8.3	mg/L		
BOD: Biochemical Oxygen Demand, 5-day	mg/L	Residue: Total (*Total Solids*)	mg/L
cBOD: Carbonaceous BOD, 5-day	mg/L	Residue: Volatile/Fixed, Total	mg/L
Coliform: Fecal MF	/100ml	Residue: Suspended (*Suspended Solids*)	mg/L
Coliform: Total MF	/100ml	Residue: Volatile/Fixed, Suspended	mg/L
Coliform: Tube Fecal	/100ml	TDS - Total Dissolved Solids	mg/L
Coliform: Tube Total	/100ml		
Specific Conductance, at 25 °C	umhos/cm		
Turbidity	NTU		
		Other Parameters:	
		pH	s.u.

LAB COMMENTS :

Field Parameters(optional):	Water Temp (°C):	pH (s.u.):	Dissolved Oxygen (ppm):	Conductivity (µmhos/cm):	Salinity (ppt):

Revision: 2/06/2015

Figure 7.3. Underground Storage Tank Field Sheet



UNDERGROUND STORAGE TANK SECTION
FIELD/LAB FORM

NORTH CAROLINA
Dept. of Environment and Natural Resources
Division of Waste Management - UST Section

COUNTY :
QUAD NO:
LATITUDE :
LONGITUDE:

SAMPLE PRIORITY
☐ ROUTINE ☐ EMERGENCY

☐ CHAIN OF CUSTODY

REPORT TO : UST - Regional Office
COLLECTOR(S) :
DATE:
TIME:

SAMPLE TYPE
☐ Soil
☐ Water
☐ Other

Location code:

Lab Number :
Date Received :
Time Received :
Received By :

Released By :
Date reported :

PURPOSE (circle): Baseline, Complaint, Compliance, LUST, Pesticide Study, Federal Trust, Other:

Field Analysis

pH _____ units Spec. Cond. at 25°C _____ umhos/cm2 Owner:
Odor _____ Temperature _____ °C Location or Site:
Description of sampling point:
Appearance _____ Sampling Method: (Pump, bailer, etc.)
Field Analysis by _____ Remarks: (pumping time, air temp., etc)

LABORATORY ANALYSIS

☐ BOD	☐ Dissolved Solids	☐ Ag-Silver	☐ Organochlorine Pesticides
☐ COD High	☐ Fluoride	☐ Al-Aluminum	☐ Organophosphorus Pesticides
☐ COD Low	☐ Hardness, total	☐ As-Arsenic	☐ Nitrogen Pesticides
☐ Coliform: MF Fecal	☐ Hardness, (non-carb)	☐ Ba-Barium	☐
☐ Coliform: MF Total	☐ Phenols	☐ Ca-Calcium	☐ Acid Herbicides
☐ TOC	☐ Specific Conductivity	☐ Cd-Cadmium	☐
☐ Turbidity	☐ Sulfate	☐ Cr-Chromium *	☐ Semivolatiles
☐ Residue, Suspended	☐ Sulfide	☐ Cu-Copper	☐ TPH-Diesel Range
☐	☐ MBAS	☐ Fe-Iron	☐
☐	☐ Oil and Grease	☐ Hg-Mercury	☐ Volatile Organics (VOA bottle)
☐ pH	☐ Silica	☐ K-Potassium	☐
☐ Alkalinity to pH 4.5	☐ Boron	☐ Mg-Magnesium	☐ TPH-Gasoline Range
☐ Alkalinity to pH 8.3	☐ Formaldehyde	☐ Mn-Manganese	☐ TPH-BTEX Gasoline Range
☐ Carbonate	☐ NH3 as N 610	☐ Na-Sodium	☐
☐ Bicarbonate	☐ TKN as N 625	☐ Ni-Nickel	☐
☐ Carbon dioxide	☐ NO2 +NO3 as N 630	☐ Pb-Lead *	☐
☐ Chloride	☐ P Total as P	☐ Se-Selenium	☐
☐ Chromium, Hex	☐ PO4	☐ Zn-Zinc	☐
☐ Color: True 80	☐	☐	☐
☐ Cyanide	☐	☐	Temperature on arrival (°C):

* Metals analyses of groundwater samples (excluding Mercury) require Standard Methods 3030C Preliminary Treatment for Acid Extractable Metals.

COMMENTS:

UST-54 REV. 1/06

USTFieldsheet-20070209-DWQ-LAB-OPS

Figure 7.4. Water Quality Sediment, Soil and Tissue Field Sheet

DIVISION OF WATER RESOURCES

SURFACE WATER SEDMENT/TISSUE FIELDSHEET

For Lab Use ONLY

Lab Number:	
Date Received:	Time:
Rec'd by:	From: Bus-Courier-Hand Del.
DATA ENTRY BY:	CK:
DATE REPORTED:	

COUNTY: _____
RIVER BASIN: _____
REPORT TO: ARO FRO MRO RRO WaRO WiRO WSRO TS AT BM
Other_____
SHIPPED BY: Bus, Courier, Staff, Other_____
COLLECTOR(S): _____
LOCATION CODE: _____
LATITUDE: _____ LONGITUDE: _____

◯ Sediment ◯ Soil ◯ Tissue

STATION LOCATION: _____
REMARKS: _____

Station #	Date Begin (yy/mm/dd)	Time Begin	Date End (yy/mm/dd)	Time End	Depth DM DB DBM	Value Type A H L	Composite T S B	Sample Type C G GNXX

*For parameters not listed on this fieldsheet, verify capability with the laboratory then write the requested analyses in the appropriate column.

		Tissue*	Units		Sediment/Soil*	Units		Tissue*	Units		Sediment/Soil*	Units		Tissue*	Units		Sediment/Soil*	Units
1		As – Arsenic	mg/kg		Ag – Silver	mg/kg		Chlorinated Pest									Oil and Grease	
2		Al - Aluminum	mg/kg		Al - Aluminum	mg/kg		PCBs									TOC	
3		Cd – Cadmium	mg/kg		As – Arsenic	mg/kg		PBBs										
4		Cr – Chromium	mg/kg		Cd – Cadmium	mg/kg												
5		Cu – Copper	mg/kg		Cr – Chromium	mg/kg												
6		Fe – Iron	mg/kg		Cu – Copper	mg/kg												
7		Hg – Mercury	mg/kg		Fe – Iron	mg/kg												
8		Mn – Manganese	mg/kg		Hg – Mercury	mg/kg												
9		Ni – Nickel	mg/kg		Mn – Manganese	mg/kg												
10		Pb - Lead	mg/kg		Ni – Nickel	mg/kg												
11		Se – Selenium	mg/kg		Pb - Lead	mg/kg												
12		Zn – Zinc	mg/kg		Se – Selenium	mg/kg												
13					Zn – Zinc	mg/kg												
14					Ca - Calcium	mg/kg												
15					K - Potassium	mg/kg												
16					Mg – Magnesium	mg/kg												
17					Na – Sodium	mg/kg											Fish species (p84005)	
18																	Fish species – Numeric (p74990)	
19																	Temperature on arrival (°C):	
20																		

	Sample Wt. (g)	Length (cm)		Sample Wt. (g)	Length (cm)		Sample Wt. (g)	Length (cm)		
1			5			9			◯	WHOLE FISH
2			6			10			◯	FILLET
3			7			11			◯	VISCERA
4			8			12			◯	SHELLFISH
									◯	OTHER

Revision 08.23.2013

Figure 7.5. Water Quality Section Surface Water Chain of Custody Form

Report to: _____DIVISION OF WATER RESOURCES– WATER QUALITY SECTION Surface Water

Page _____ of _____

CHAIN OF CUSTODY RECORD

NC /DWR WSS LABORATORY (check one): [ ] CENTRAL [ ] ARO

For Investigation of:						**Incident No.**
Sample collector (print name) _____ And DM-1forms completed by: _____ Sample collector's signature:_____						
Field storage conditions and location (when applicable):						
Lab Use Only LAB NO.	SAMPLE ID	QUAD. NO.	LOCATION	DATE SAMPLED	TIME SAMPLED	NUMBER OF CONTAINERS

Relinquished by (signature):	Date	Time	Received by (signature):	Date	Time
Relinquished by (signature):	Date	Time	Received by (signature):	Date	Time
Relinquished by (signature):	Date	Time	Received by (signature):	Date	Time

Method of Shipment (circle one): State Courier Hand-delivered Federal Express UPS Other: _____

Security Type and Conditions:	Sealed by:	Broken by:

INTRALABORATORY CHAIN OF CUSTODY - Lab Use Only

LAB NUMBERS FROM	THROUGH	NUMBER BOTTLES	ANALYSES REQUESTED	RELINQUISHED BY:	RECEIVED BY:	DATE	TIME

8.0 ANALYTICAL PROCEDURES

The analytical methods utilized by the laboratory are listed in Section 5.0 of this QAM. Whenever possible, only EPA-approved methods are used. The reference methods are also documented in the laboratory's Standard Operating Procedures (SOPs). For information about the documentation and maintenance of laboratory SOPs, refer to SOP# QAG001 - *Guidance for Preparing Standard Operating Procedures*.

8.1 Reference Methods

The following compilations encompass the individual methods listed in Section 5.0 (listed by acronym designation as used in Section 5.0 tables).

8.1.1 EPA

- *Methods for Chemical Analysis of Water and Wastes;* USEPA Office of Research and Development, Cincinnati, OH, 3/83; EPA 600/4-79-020.

- *Methods for the Determination of Metals in Environmental Samples*, USEPA Office of Research and Development, Washington DC, 6/91, EPA/600/4-91/010.

- *Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW-846*; 3rd edition (9/86), with Final Updates I (7/92), II (9/94), IIA (9/93), IIB (1/95) ,III (12/96);and IV(2007) USEPA Office of Solid Waste and Emergency Response, Washington, D.C.

- *Method for the Determination of Organic Compounds in Drinking Water, Supplement I*, EPA 500/4-90/020, July 1990.

- *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office, Washington, D.C., July 1993. [

- Standard Methods – Examination of Water and Waste Water On-Line

8.1.3 Other Reference Procedures

Other reference procedures for non-routine analyses may include methods established by a specific state or by a vendor company such as HACH, QUIK CHEM or by organizations such as USGS or ASTM. Sample type, source, instrumentation and the governing regulatory agency requiring the analysis will determine the method utilized.

8.2 Method Modifications

Many of the environmental sample analysis methods were written using the best available technology at the time of their publication. However, some of these methods have not been updated since that time and therefore do not reflect advances in technology. Additionally, 40 CFR Part 136.6 allows for method modifications that lower detection levels, improve precision, reduce interferences, lower lab costs and promote environmental stewardship by reducing generation of lab wastes. The Water Sciences Section has modified some methods to accomplish these goals and to take advantage of technological advances. The majority of these modifications are minor, do not have any impact on the quality of the data, and are included here for the sake of completeness. Some published methods are also not clear or are ambiguous about their requirements. Clarifications are made about these methods in this Section.

All modified methods are verified by performing an MDL and IDOC study and are closely monitored for precision, accuracy and bias attributed to matrix. If the method performance is equivalent to that published in the method, the modification is adopted for routine use in the laboratory. The modification is summarized in the QAM and is described in detail in the SOP.

The following modifications (8.2.1 – 8.2.10) have been made to the methods in Table 5.1:

8.2.1 EPA 200.2

Method 200.2 (hot plate) is modified and validated for use with a block digester. 0.50 mL of nitric acid and 0.50 mL of 1+1 hydrochloric acid is added to 50 mL of sample in either a Teflon or disposable polypropylene tube and heated at 95°C for approximately 6 hrs. The sample is then brought back to a volume of 50 mL with deionized water. U.S. EPA Region 4 has provided written approval for the use of EPA Method 200.2 with this modification.

8.2.2 EPA 245.1

The QCS is not used to fortify an aliquot of LRB or sample matrix (ref. EPA Method 245.1, Section 3.11). Hydrochloric acid is used instead of sulfuric acid to prepare the stannous chloride solution as stated in Section 7.10. Stannous chloride is prepared per instructions from the instrument manufacturer. The lab is analyzing an LFM and LFMD to monitor precision (instead of LD_1 and LD_2 as stated in EPA Method 245.1, Section 3.5). The relative percent difference will determine if precision is acceptable.

8.2.3 EPA 245.6

An aqueous QCS is analyzed in addition to the SRM (ref. EPA Method 245.6, Section 3.10). Hydrochloric acid is used instead of sulfuric acid to prepare the stannous chloride solution as stated in Section 7.7. Stannous chloride is prepared per instructions from the instrument manufacturer. The "Stock Standard Solution" defined in Section 4.3 of SOP# MTA005R0 is equivalent to the "Mercury Stock Standard" required in EPA Method 245.6, Section 7.3. Calibration standards are prepared by diluting the stock standards solution and not by fortifying tissue samples as stated in Section 9. Potassium persulfate is not used in digesting tissue samples, as stated in Section 11.2. This deviation is based on historical data and percent recovery from analysis of a SRM.

8.2.4 EPA 245.5

An aqueous QCS is analyzed in addition to the SRM (ref. EPA Method 245.5, Section 3.10). Hydrochloric acid is used instead of sulfuric acid to prepare the stannous chloride solution as stated in Section 7.7. Stannous chloride is prepared per instructions from the instrument manufacturer. The "Stock Standard Solution" defined in Section 4.3 of SOP# MTA006R0 is equivalent to the "Mercury Stock Standard" required in EPA Method 245.5, Section 7.3. Sediment samples are not preserved with nitric acid as stated in EPA Method 245.5, Section 8.2. This is to comply with preparation of sediment samples for other metals using EPA Method 200.2, Section 8.2.

8.2.5 Standard Methods 5220 D-1997

Standard Methods 5220 D-1997 allows the use of alternative digestion vessels and reagents (see Standard Methods 5220 D-1997 2 (a) and 5220 C-1997 2 (a)). Hach Company's digestion vessels, reagents and reactor are used to digest samples. The sample digestates are transferred from the Hach reaction tubes to 1.0-cm spectrophotometer cells for colorimetric determination on the Shimadzu spectrophotometer. The modification has been validated through MDL and IDOC studies and ongoing digested QC standards.

8.2.6 ASTM D 6303-98

ASTM D 6303-98 Section 8.6.1.8 requires replicate measurements to agree to within 0.3%. This criterion would not allow a drop difference. The laboratory believes this to be a typographical error and has written the SOP to state “Replicates should agree to within 0.3 ml.”

8.2.7 EPA Method 445.0

The pigments are extracted from the phytoplankton using 10 ml 90% acetone solution (rather than 4 ml as specified in the method section 11.1.1) with the aid of a mechanical tissue grinder and allowed to steep (refrigerated) for a minimum of 2 hours, but not to exceed 24 hours, to ensure thorough extraction of the chlorophyll *a*.

8.2.8 EPA Method 625

Extracts of Base Neutrals and Acids are combined during extraction. The pH extraction sequence is reversed to better separate acid and neutral components. Alternate calibration curve other than those specified in the method is utilized. U.S. EPA Region 4 has provided written recommended approved Modification to EPA Method 625. Please see figure 8.1 EPA Memorandum Recommended Approved Modification to EPA Method 625 – November 1, 2006

8.2.9 SW-846 Methods 8081B and 8082A

GC/MS confirmation is applied for doubtful identification only and additional parameters have been added to the analyte list.

8.2.10 SW-846 Method 8141B

The expiration date for standards is one year and additional parameters have been added to the analyte list.

8.2.11 SW-846 Method 3550C

Extraction of Fish Tissues for Organochlorine Pesticides and PCBs uses five grams of homogenized, ground tissue is mixed with sodium sulfate, then soxhlet extracted with methylene chloride. The extract is concentrated and cleaned-up by Gel Permeation Chromatography (GPC).The resulting extract is analyzed by capillary GC using electron capture detection (ECD).

8.3 Alternative or New Methods

When alternative procedures are employed or in cases where a test method is not mandated by regulation, the lab may choose to incorporate a new method or new instrumentation. Prior to sample analysis; however, the lab must meet the relevant start-up, calibration and ongoing validation and QC requirements. For regulated monitoring, an alternate test must be procured from EPA Region 4. An alternate test procedure is one that differs from a method previously approved by the U.S. EPA for determining the constituent of interest in National Pollutant Discharge Elimination System (NPDES) monitoring. The methods developed in-house and either validated or approved by Region 4 are outlined below:

8.3.1 ASTM D 6303-98

This method covers the determination of the formaldehyde monomer concentration in water and wastewater.

8.3.2 SM 3030C-2004

This method is no longer used for digesting Groundwater Section's monitoring well samples per memoranda, "Aquifer Protection Section Policy for Metals Determinations Required by 15A NCAC 2L", May 13, 2013, Jay Zimmerman, PG, Aquifer Protection Section Chief. A copy of this memorandum is included as Figure 8.2.

8.3.3 EPA 200.2

U.S. EPA Region 4 has provided written approval to the NC DWR Water Sciences Section for the use of EPA 200.2 for NPDES compliance monitoring. A copy of this document is included as Figure 8.3.

8.3.4 EPA 200.8

U.S. EPA Region 4 has provided written approval to the NC DWR Water Sciences Section for the use of EPA 200.8 for NPDES compliance monitoring. A copy of this document is included in Figure 8.4 and an electronic mail notice of clarification regarding this approval is included as Figure 8.5.

8.3.5 EPA 200.9

U.S. EPA Region 4 has provided written approval to the NC DWR Water Sciences Section for the use of EPA 200.9 on wastewater. A copy of this document is included as Figure 8.6.

8.3.6 Platinum-Cobalt Color (SM2120 B-2001)

U.S. EPA Region 4 has provided written approval to the NC DWR Water Sciences Section for the use of a spectrophotometer operating at a wavelength of 460 nm in place of the visual comparison method for wastewater samples. A copy of the request for approval and EPA's approval document are included as Figures 8.7 and 8.8.

8.4 Standard Operating Procedures

The DWR Water Sciences Section Laboratories have developed Standard Operating Procedures (SOPs) for all analytical procedures and laboratory operations. The analytical SOPs are derived from the most recently promulgated/approved published method. SOPs are an integral part of a successful quality system and facilitate consistency in the reliability and integrity of an end result. A SOP should describe the activity or analytical method used in the laboratory in sufficient detail that a competent analyst unfamiliar with the method could conduct a reliable review or obtain acceptable results. Each analytical test method SOP contains the following (where applicable): method title and reference method, authorization signatures and approval dates, applicable matrices, scope and application, components to be analyzed, procedure summary, deviations from referenced method, definitions, interferences, safety and waste handling, apparatus and equipment, reagents and standards, sample collection, preservation, shipment and storage, calibration and standardization, sample preparation, sample procedure, calculations, quality control, data validation procedures, preventive maintenance, troubleshooting and corrective actions for out-of-control or unacceptable data, referenced documents, personnel qualifications, attachments (including tables, diagrams, flowcharts, benchsheets, etc.), and revision history. Non-analytical SOPs follow a similar format where possible.

General quality assurance SOPs are approved by the Environmental Program Supervisors and the QAO or a member of the SOP Committee. All SOPs are controlled in the laboratory: numbered sequentially, approved and signed by the Environmental Program Supervisor and QAO or SOP Committee member after review, dated with an effective date, placed in controlled manuals or placed in a read-only format on the network, and archived when updated. The procedures for document control shall also apply to SOPs that are being used, but are designated as 'DRAFT' versions. Procedures for preparation, review, revision and control of SOPs are incorporated by reference to current revision of SOP# QAG001, Guidance for Preparing Standard Operation Procedures (SOPs) SOPs are dynamic documents and may supersede some requirements in this document until the QAM annual update. SOPs must accurately reflect the operations of the Water Sciences Section Laboratories at any given time. They must be updated, verified and re-approved anytime procedures change. If no changes have taken place, SOPs must be reviewed at least annually. Any revisions must follow the prescribed approval process.

8.5 Requirements for Methods Start-up

Before the laboratory may institute a new method and begin reporting results, it must write a SOP, demonstrate satisfactory performance, and conduct a method detection limit study. There may be other requirements as stated within the published method or regulations (i.e., retention time window study, IDL, ATP approval from EPA R4, etc.).

In some instances a situation may arise where a client requests that an unusual analyte be reported using a method where this analyte is not normally reported. If the analyte is being reported for regulatory purposes, the method must meet all procedures outlined within this QAM (i.e., SOP, MDL, and IDOC). If the sample is not for legal or regulatory purposes, the result may be reported as long as the following criteria are met: 1) the instrument is calibrated for the analyte to be reported using the criteria for the method and ICV/CV criteria are met, 2) the reporting limit is set at or above the first standard of the curve for the analyte and 3) the process is documented.

8.5.1 Initial Demonstration of Capability (IDOC)

An initial demonstration of capability (IDOC) must be made prior to using any test method to report results, and at any time there is a significant change in instrument type, personnel or test method.

Note: In laboratories with specialized "analytical units" (a well-defined group of analysts that together perform the method analysis), the group as a unit may meet the above criteria and this demonstration must be fully documented.

In general, this demonstration does not test the performance of the method in real world samples, but in the applicable and available clean matrix, e.g., water, solids or biological tissue. Actual sample spikes may also be used for this purpose, but only prior to reporting analytical results and only if the data was generated within the last twelve months. For analytes that do not lend themselves to spiking, e.g., TSS, the demonstration of capability may be performed using quality control samples or other predetermined regiment for demonstrating proficiency in a given test method. Specific guidance on demonstration of capability may be included in the methods or as required by the analytical unit.
Demonstrations shall be documented through the use of the IDOC Certification Statement form in Figure 4.5 or similar format. Summary results should include analyst, date, method, matrix, instrument identification or serial number, preparatory method or clean-up procedures used, SOP numbers, any method specific criteria, analyte(s), spike concentration, units of measurement, replicate values, mean % recovery, mean value, population (n-1) standard deviation of recovery, % relative standard deviation of recovery, acceptance criteria, a reference for this criteria, laboratory reagent blank data and approval signatures.

The following steps, which are adapted from the EPA test methods published in 40 CFR Part 136, Appendix A, shall be performed for IDOC certification.

a) A quality control sample shall be obtained from an outside source (i.e., standard/certified reference materials). If not available, the spiking standard may be prepared by the laboratory using stock standards that are prepared independently from those used in instrument calibration (e.g., matrix spike or laboratory control spike).

b) The analyte(s) shall be diluted in a volume of clean matrix sufficient to prepare at least four aliquots at a concentration (1) specified by a method; or if unspecified; (2) approximately 5 to 50 times the method-stated or laboratory-calculated practical quantitation limit (PQL); or (3) at approximately mid-range in the calibration curve.

c) At least 4 aliquots shall be prepared and analyzed according to the test method either concurrently or over a period of days. Each analyst performing the IDOC must perform each of the steps required to perform the method (except in specialized analytical units as described above). Non-routine procedures (e.g., specialized clean-up procedures) should also be demonstrated for each analyte and each method where applicable.

d) Using all of the results (generally the raw data results are used without rounding as when reporting), calculate the mean recovery in the appropriate reporting units and the standard deviations of the population sample (n-1), in the same units, for each parameter of interest. When it is not possible to determine mean and standard deviations, such as for presence, absence and logarithmic values, the laboratory will assess performance against criteria described in the Method SOP.

e) Compare the information obtained from (d) above to the corresponding mandated acceptance criteria for precision and accuracy in the test method (if applicable) or to laboratory-generated acceptance criteria (LCS or interim criteria) if there is no mandatory criteria established. If any one of the parameters do not meet the acceptance criteria, the performance is unacceptable for that parameter.

f) When one or more of the tested parameters fail at least one of the acceptance criteria, the analyst must either:
   - Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with c) above; or
   - Beginning with c) above, repeat the test for all parameters that failed to meet criteria. Repeated failure; however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with c) above.

g) At least one Laboratory Reagent Blank (LRB) shall be included with the IDOC study data. When data is gathered over a period of days, the associated LRB for each day's analysis shall be included.

h) A Certification Statement shall be used to document the completion of each IDOC. A copy of the certification is archived in a method/instrument folder and a copy is archived in the analyst's training folder.

i) Methods on line prior to the effective date of this Section shall be updated to the procedures outlined above as new analysts perform their demonstration of capability. A copy of the new record will

replace that which was used for documentation in the past. At a minimum the precision and accuracy of four mid-level laboratory control samples must have been compared to the laboratory quality control acceptance limits.

8.6 Laboratory Reagent Water

Laboratory reagent water is used for the preparation of reagents and standards (e.g., calibration standards, spike solutions, standard reference solutions), the dilution of samples, and blank analysis. Reagent water should have no detectable concentration of the compound or element to be analyzed at detection limit of the analytical method. Reagent water must be free of substances that interfere with analytical methods. Laboratory reagent water is prepared by passing tap water (City of Raleigh) through a system of filters to produce deionized water, which should consistently meet or exceed the American Society for Testing and Materials (ASTM) Type II Reagent Grade Water requirements. The deionized water system is comprised of a fibrous pre-filter, 1 carbon tank, and 3 resin tanks; the system is serviced on a monthly basis by an outside vendor. The parameter measured to verify the quality of the deionized water is conductivity. The conductivity is checked and recorded at least monthly and must be <1 megohm-cm at 25ºC; in addition, the deionized water system includes a conductivity indicator light which is checked and recorded daily. If the water's conductivity does not meet the specified requirement, or the indicator light is not illuminated, then the Support Unit must be notified immediately in order to initiate arrangements for service of the system and correction of the issue.

Reagent water used in the Volatile Organics Unit is obtained from a non-chlorinated well and passed through an activated charcoal filter. Semivolatiles Organics Unit reagent water is from a non-chlorinated well.

For certain analytical parameters, additional treatment of the deionized water is necessary and is accomplished by use of counter-top water purification systems. These systems consist of a series of four treatment cartridges and a fiber filter through which deionized water is fed, and re-circulate every 15 minutes. The systems measure and display the resistivity of the produced water, which is read and recorded on a daily basis. The acceptable range for produced water is 17.9 to 18.3 megohm-cm. Filters should be replaced as needed, or at a minimum prior to the expiration date printed on the cartridges.

8.7 Reagents and Standards

The nature of the analytical laboratory demands that all material used in any of the procedures is of a known quality. All standards and reagents are prepared from reagent grade materials, primary standards. Standards may also be purchased from a reputable vendor at a known concentration. Standards and reagents are prepared using balances in which the calibration is verified daily or on date of use, Class A volumetric glassware or pipettors which have been calibrated in accordance with ISO 8655-6, and ASTM Type II reagent water. The wide variety of materials and reagents available makes it advisable to specify the name, brand, and grade of materials to be used in any determination. This information is contained in the method SOP. The material is dated and initialed upon receipt and upon opening.

Safety Data Sheets (SDS) are kept in a central location known to all personnel. Anyone may review these for relevant information on the safe handling and emergency precautions of chemicals used and stored on-site. Each analytical unit keeps a notebook of pertinent SDS for all chemicals used in that unit for immediate access. In addition, laboratory SOPs describe precautionary measures (listed in the *Safety and Waste Handling* section and at the critical steps in the procedure) for particularly hazardous chemicals and known or suspect carcinogens.

8.7.1 Specifications

There are many different grades of analytical reagents available to the analyst and most methods in use in the laboratory specify the grade of reagent that must be used in the procedure. If the quality of the reagent is not specified, it may be assumed that it is not significant in that procedure and; therefore, any grade reagent may be used. It is the responsibility of the analyst to check the procedure carefully for the suitability of the reagent grade.

Records of manufacturer's certification and traceability statements are maintained in files or binders in each analytical unit. These records include date of receipt, lot number (when applicable) and expiration date (when applicable). Commercial materials purchased for preparation of calibration solutions, spike solution, etc., are usually accompanied with an assay certificate or the purity is noted on the label. If the assay purity is 96% or better, the weight provided by the vendor may be used without correction. If the assay purity is less than 96% a correction will be made to concentrations applied to solutions prepared from the stock

commercial material. Wherever possible, standards must be traceable to NBS/NIST standards. Records to that effect are maintained in the area in which the standard is to be used.

Logbooks are utilized to document all information needed to maintain proper traceability of all standards and reagents prepared or purchased by the Laboratory. Logbooks document the date of preparation or opening of purchased material, expiration date, a list of standards/reagents or solutions used, lot numbers and the preparer's name. Calibrated instruments (e.g., balance or auto pipette) used in the preparation of standards must be identified in the logbook by serial or assigned ID number. Additional information, such as pH, may also be recorded. For purchased standards/reagents, the logbook is used to record the vendor, date opened, lot number and expiration date.

Reagents or working standards that are prepared in-house shall be recorded in a logbook, dated, initialed by the analyst preparing the reagent or standard, and is assigned a unique designation for tracking purposes. All reagents and solutions in the laboratory areas shall be labeled to indicate; at a minimum, identity, titer or concentration, solvent (when applicable), preparation date, preparer's initials and expiration date. If a vial or container is too small for all the information listed above, use an ID number to link the vial to the logbook entry containing this information.

Deteriorated or outdated reagents and solutions shall not be used. Expiration dates for standards and reagents are usually specified in the methods or by the manufacturer and are adhered to unless degradation prior to this date is observed. Deterioration may be recognizable by changes in physical appearance such as a change in color or clarity, a change in volume, clumping or the formation of solids. Purchased materials are labeled with the date received and the date opened. Reagents are stored according to method or manufacturer's instructions and discarded per the appropriate SOP or the laboratory Chemical Hygiene Plan upon expiration.

When expiration dates are not specified, the following guidelines are used:

- Stock Standards for calibration can be used for up to one year if properly preserved and stored. Standard solutions, such as ammonia and TKN standards, may need to be prepared more frequently. Mixed stock standards such as those used for metals analyzed by EPA Methods 200.7 and 200.8 are prepared every six months.
- Titrating solutions need to be either restandardized or a new bottle of vendor-certified standard opened each month. Titrating solutions used by the Water Sciences Section include 0.02*N* sulfuric acid (alkalinity), EDTA (hardness), 0.025*N* sodium thiosulfate (phenol), and 0.1*N* HCl (formaldehyde).
- Calibration or spiking standards are dilutions of stock standards used to calibrate an instrument. These standards are to be prepared daily **unless specified otherwise in the method SOP.**
- Acids can be used for up to three years; however, additional care must be taken with nitric and sulfuric acid, as exposure to sun and heat will accelerate decomposition.
- Organic solvents may be used for up to one year.
- Dry, inorganic reagents and specially denatured alcohol formulations may be used for up to five years.

All other solutions for which no expiration date is specified are used for no more than a year. They are valid for that length of time only if evaporation is minimized and proper preservation and storage techniques are used. If a bottle is opened often or is much less than half full more frequent replacement may be required. If a solution, such as a buffer, is expected to degrade rapidly after opening, it will be labeled with the date opened and an adjusted expiration date based on the date opened. Solutions are always poured off from the original bottle and unused portions are never returned to the original bottle. If degradation becomes apparent the solution is discarded immediately and the time period of valid use (holding time) for that solution is reduced.

The stability of standard solutions can be demonstrated by comparing the analysis of freshly prepared solutions periodically with older preparations. The age of the standards must be limited using expiration dating so that no significant difference can be detected between older solutions and freshly prepared

solutions. The lab analyst may also refer to the decomposition data available on a chemical's Safety Data Sheet.

Attempts should be made to control the quality of chemicals by purchasing in quantities fitting for the volume to be used. Smaller containers are appropriate for low-volume use and for products that have short shelf life while larger containers may be appropriate for high-volume use and products with indefinite shelf life.

8.7.2 Chemical Storage

All reagents and solvents are dated upon receipt. (See Section 8.7.1 for procedures) All manufacturer expiration dates are observed. If an expiration date is not specifically stated on the manufacturer's label, a holding time may be assigned and the expiration date written on the label. The date the reagent was opened is also written on the label.

All reagents and solvents must be stored based on safety and storage considerations, as well as ease of access and proximity to primary location of use. Safety and storage guidelines for a chemical can be found in the Safety Data Sheet (SDS) and container labels. In addition, specific safety and storage information is included in all laboratory SOP's. Chemical compatibility must be reviewed prior to storing chemicals in close proximity to each other.

Proper storage of chemicals may include refrigeration, storage in darkness or in an amber glass container, protection from moisture (desiccator), specialized cabinets (flammables or acids), or ventilation. Proper storage of chemicals helps to prevent degradation of the chemical or solution and reduce potential hazards.

Acids, except portions that are dispensed into small, labeled containers for immediate use, are stored in the original containers in the operational area in an acid cabinet or in the chemical supply room separate from alkaline bases and other unsuitable chemicals as stated in the SDS.

Bases, except portions that are dispensed into small, labeled containers for immediate use, are stored in the original containers in the operational area or in the chemical supply room separate from acids.

Solvents, except portions that are dispensed into small, labeled containers for immediate use, are stored in the original containers in a separate area of the chemical supply room designated for solvent storage or in vented, explosion-proof cabinets in the operational area.

Dry reagents and vendor-prepared solutions are stored in designated areas in each laboratory unit. The general storage areas in the lab units are maintained at room temperature; some cabinets below fume hoods are ventilated.

Organic extracts and stock solutions are stored in a freezer in the appropriate operational unit. Working solutions are refrigerated or frozen as necessary. Neat standards are stored at room temperature in the analytical area. Inorganic digestates, distillates and stock and working solutions may either be refrigerated or stored at room temperature. Instructions are detailed in the analytical SOP.

8.8 Waste Disposal Methods

The Water Sciences Section Chemistry Laboratory collects and disposes of wastes in a manner which ensures compliance with all federal, state, and local laws, regulation, and ordinances. Procedures are designed to minimize employee exposure to hazards associated with laboratory-generated wastes and to afford maximum environmental protection. Waste handling procedures are detailed in the laboratory SOPs and Chemical Hygiene Plan (CHP).

A waste is a hazardous waste if it is listed in 40 CFR Part 261.30-261.33 or fails any of the criteria in 40 CFR Part 261 Subpart C. Personal knowledge of the waste's characteristics must also be considered. Hazardous wastes must be segregated, labeled appropriately, stored in a designated waste disposal area, and disposed of by a commercial waste disposal company. The Laboratory Safety Officer is responsible for maintaining the on-site system to prepare the wastes for disposal, scheduling

removal by the contractor, maintaining records, and assuring that the contractor is permitted by the NC Division of Waste Management. The selection of a waste disposal contractor must be predicated on their being permitted to transport hazardous wastes coupled with an absence of RCRA/DOT violations and a proven record of successful performance.

Processes generating organic solvent wastes in the laboratory include semi-volatile, herbicide, and pesticide sample extractions and preparations, sample extractions for Wet Chemistry parameters (e.g., chlorophyll *a*, MBAS, Oil and Grease), and standard/reagent preparation. Laboratory solvent wastes are stored in labeled four-liter or 2.5 liter glass bottles. These containers are stored closed in fume hoods or flammable liquids cabinets in the appropriate analytical units.

At the Central Laboratory, the contents of solvent waste bottles are periodically transferred into a 55-gallon drum labeled "Hazardous Waste" and "Flammable Liquid." The solvent waste drum is located in the solvent storage room, (G102) and maintained by the laboratory in compliance with RCRA regulations for disposal of waste solvents. All records of waste disposal are maintained, and include solvent waste drum logs, waste disposal manifests, correspondence from disposal firms and any other information necessary to document the disposal of laboratory wastes. Organic solvents containing PCBs are segregated for separate disposal with the appropriate manifest.

Solvent extracts are stored chronologically in appropriate refrigerators in the laboratory units. Upon expiration of required holding times, sample extracts are disposed of by pouring the extract into the appropriate solvent storage container and placing the empty extract container into the appropriate solid waste container.

Other chemicals and hazardous wastes are collected and stored in the acid storage room (G106) or solvent storage room. Chemicals and waste are segregated by hazardous class and held until removed for disposal by a commercial waste disposal company.

Only completed samples (including raw samples, extracts, and digestates) with authorized reports (checked from DWR LABWORKS™ LIMS) are disposed. The Central Laboratory has a two-stage sewage system. Laboratory drains are separated from the sanitary drains. The sink and fume hood drains in the laboratory rooms converge and the water waste passes through a fiberglass tank filled with 9,000 pounds of limestone (calcium carbonate). The limestone serves to neutralize acidic and basic water wastes prior to entering the City of Raleigh's sanitary sewer system. The sanitary drains bypass this pretreatment phase and drain directly to the sanitary sewer system. Non-hazardous, aqueous samples are discarded into laboratory sink drains while flushing with tap water. Non-hazardous solid samples are disposed of in the city garbage.

Biological wastes are placed in an autoclavable biohazard bag and sterilized prior to disposal in the city garbage.

8.9 Labware

8.9.1 Labware specifications

All volumetric glassware must be Class A. Pyrex glass or equivalent should be used where possible. For safety purposes, thick-wall glassware should be used where available.

8.9.2 Labware cleaning

The proper technique for cleaning labware depends upon the intended use of the labware being cleaned. The goal is to remove all substances from the labware that might interfere with the analysis. Generally, water-soluble substances can be removed with tap water followed with multiple rinses with laboratory-grade water. In some instances, detergent may be required. Detergent washing should be followed by a series of analyte-free water rinses.

In many cases it is appropriate for labware to be cleaned by support staff using the automatic glassware washer that is located in the receiving room. Each unit brings their rinsed glassware to receiving in white polypropylene bins. To prevent cross contamination each unit's glassware is washed separately. A heavy duty alkaline machine detergent is used in the glassware washer for cleaning the glassware. The glassware washing cycles (total time approximately 30 minutes) are as follows: prewash cycle, wash cycle, rinse cycle and finally pure rinse cycle using deionized water.

Once the glassware washer is finished, the glassware is unloaded and put back into the white bins. Prior to loading bins with clean glassware, the bins are rinsed several times with water and lined with aluminum foil, with the exception of the metals glassware which is line with paper towels to prevent contamination from the aluminum foil. The process of lining the bins indicates to the units that the glassware has been washed. The clean glassware is then returned to the units.

General procedures for cleaning laboratory glassware and other labware for specific applications are outlined in Table 8-1.

8.9.3 Labware storage

Once cleaned, labware is capped, inverted or covered for storage in a designated cabinet or drawer, away from bulk chemicals or reagents.

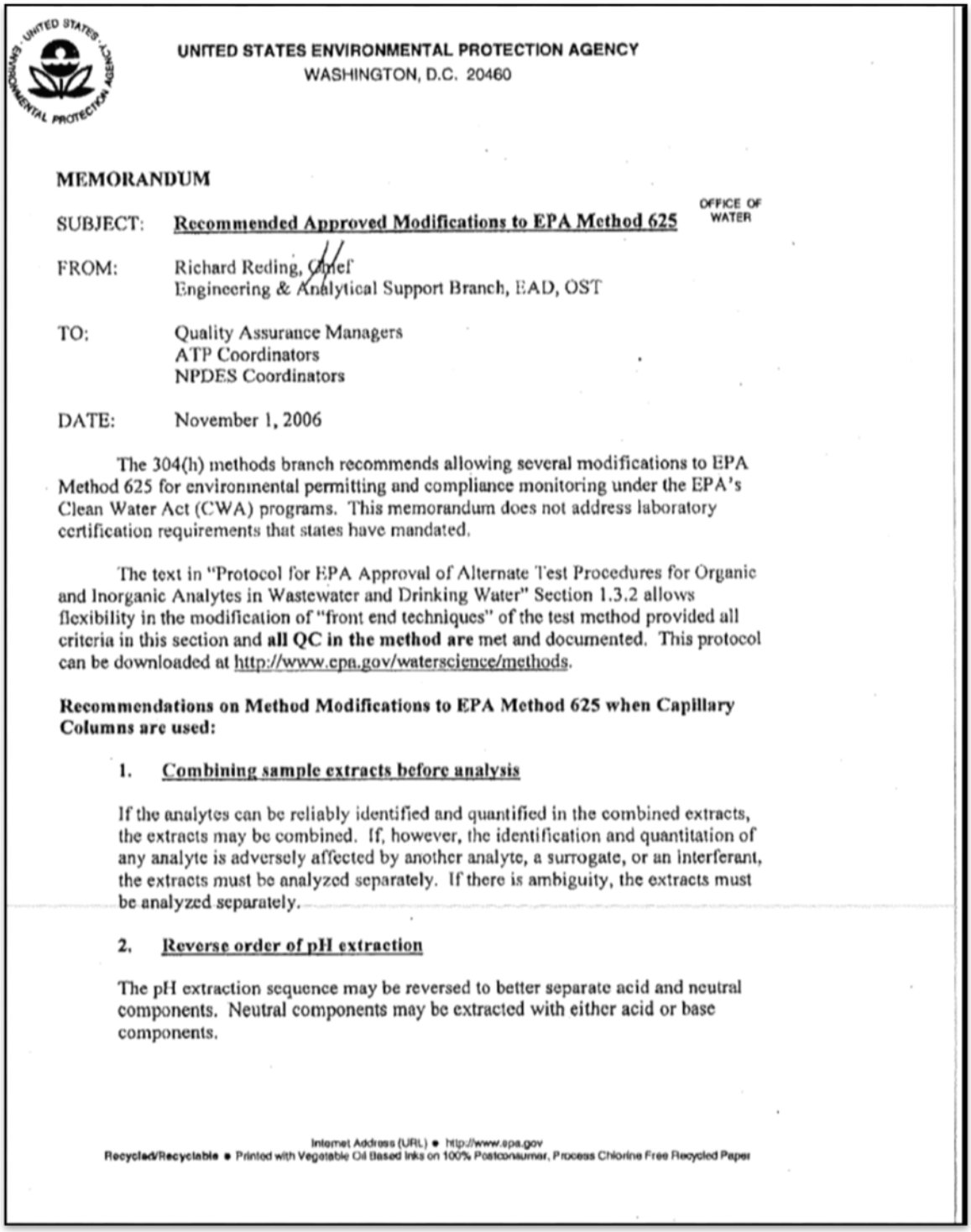
Table 8.1. Labware Cleaning Protocols.

Parameter group	Cleaning Protocols (in order specified)
Extractable Organics	1,2,4,5 (6 optional)
Purgeable Organics	1,2,4,5,6
Metals	1,2,3,4,7
Nutrients	1,2,3*, 4,7 *For nutrients, only use hydrochloric acid.
Minerals, Demand, and other Wet Chemistry	1,2,4,7
Oil and Grease	1,2,3*,4 (5,6 optional) *For oil and grease, nitric acid should be replaced by hydrochloric or sulfuric acid.
Residues	1,2,4,9
Bacteriologicals	1,2,7,8

Key to cleaning protocols:

1. Wash with hot water and a brush to scrub inside glassware and stopcocks, using a suitable laboratory-grade detergent (generally Detergent-8 which is phosphate-free or Alconox). Bacteriologicals - must pass an inhibitory residue test.
2. Rinse thoroughly with tap water.
3. Rinse with 1:1 nitric acid solution.
4. Rinse thoroughly with deionized water.
5. Rinse thoroughly with pesticide-grade acetone or methanol
6. Oven-dry at 105°C to 125°C for at least 1 hour. Note: Class A volumetric glassware should not be baked. Note: Oven dried containers (tightly capped) should remain in the oven or in a contaminant-free environment until being dispatched to the field or used for laboratory operations.
7. Invert and air-dry in contaminant-free environment.
8. Autoclave containers (the tops of which are covered with aluminum foil and an autoclave indicator strip is placed in the autoclave with the containers and tops.
9. Bake crucibles at 105°C or 180°C for 1 hour (prior to use as per method)

Figure 8.1 U.S. EPA Memorandum Recommended Approved Modification to EPA Method 625



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MEMORANDUM

OFFICE OF WATER

SUBJECT: **Recommended Approved Modifications to EPA Method 625**

FROM: Richard Reding, Chief
Engineering & Analytical Support Branch, EAD, OST

TO: Quality Assurance Managers
ATP Coordinators
NPDES Coordinators

DATE: November 1, 2006

The 304(h) methods branch recommends allowing several modifications to EPA Method 625 for environmental permitting and compliance monitoring under the EPA's Clean Water Act (CWA) programs. This memorandum does not address laboratory certification requirements that states have mandated.

The text in "Protocol for EPA Approval of Alternate Test Procedures for Organic and Inorganic Analytes in Wastewater and Drinking Water" Section 1.3.2 allows flexibility in the modification of "front end techniques" of the test method provided all criteria in this section and **all QC in the method are** met and documented. This protocol can be downloaded at http://www.epa.gov/waterscience/methods.

Recommendations on Method Modifications to EPA Method 625 when Capillary Columns are used:

1. **Combining sample extracts before analysis**

If the analytes can be reliably identified and quantified in the combined extracts, the extracts may be combined. If, however, the identification and quantitation of any analyte is adversely affected by another analyte, a surrogate, or an interferant, the extracts must be analyzed separately. If there is ambiguity, the extracts must be analyzed separately.

2. **Reverse order of pH extraction**

The pH extraction sequence may be reversed to better separate acid and neutral components. Neutral components may be extracted with either acid or base components.

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Previously, neither of these modifications has been used with Method 625 primarily because of limitations of the resolving power of the packed columns used. In 1985, EPA Region 3 Central Regional Lab requested a modification to method 625 as an alternate test procedure (ATP). Although the approval was for limit use by EPA's Region 3, Central Regional Laboratory only, this modification has come to be used throughout the laboratory community (see attached memo).

Why allow these modifications? Following the base-neutral than acid extraction sequence of method 625 in some cases demonstrated the decomposition of some analytes under basic conditions. Organochlorine pesticides may dechlorinate; phthalate esters may exchange; phenols may react to form tannates. These reactions increase with increasing pH. Reversing the extraction pH sequence may better separate acid and neutral waste components.

Other Recommended Modifications to Method 625

A smaller sample volume may be used to minimize matrix interferences provided matrix interferences are demonstrated and documented.

Alternate surrogate and internal standard concentrations other than those specified in the method are acceptable provided that method performance is not degraded;

An alternate calibration curve and a calibration check other than those specified in the method;

A different solvent for the calibration standards to match the solvent of the final extract.

Other Method Flexibility News

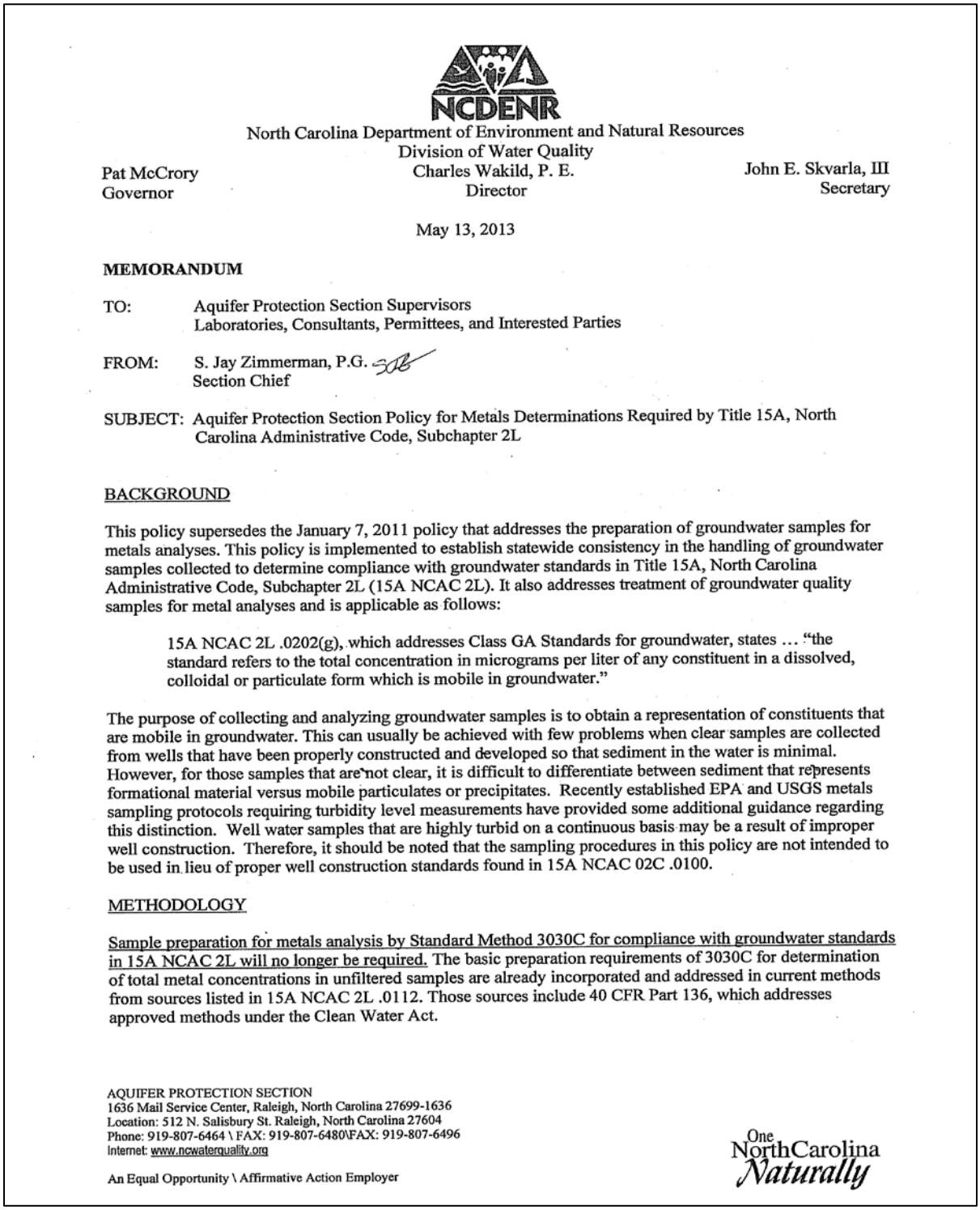
We are revising the "Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring" often referred to as the "Pumpkin Book". Many of the recommendations in the revised "Pumpkin Book" cover ways to mitigate matrix effects.

More explicit flexibility to make changes in approved methods without prior EPA approval is now described at 40 CFR Part 136.6. Such changes are only allowed if the modified method produces equivalent performance for the analyte(s) of interest, and the equivalent performance is documented. It is essential to consult the full text at 40 CFR 136.6 before undertaking method modifications.

Please feel free to forward this information. If you have any questions regarding this memorandum, please contact Lemuel Walker of EASB/EAD/OST by email at walker.lemuel@epa.gov.

cc Lemuel Walker
ATP Coordinator

Figure 8.2. Memorandum from the Aquifer Protection Section rescinding the policy for using Method 3030C for the preparation of Groundwater monitoring well samples.



North Carolina Department of Environment and Natural Resources
Division of Water Quality

Pat McCrory, Governor
Charles Wakild, P. E., Director
John E. Skvarla, III, Secretary

May 13, 2013

MEMORANDUM

TO: Aquifer Protection Section Supervisors
Laboratories, Consultants, Permittees, and Interested Parties

FROM: S. Jay Zimmerman, P.G.
Section Chief

SUBJECT: Aquifer Protection Section Policy for Metals Determinations Required by Title 15A, North Carolina Administrative Code, Subchapter 2L

BACKGROUND

This policy supersedes the January 7, 2011 policy that addresses the preparation of groundwater samples for metals analyses. This policy is implemented to establish statewide consistency in the handling of groundwater samples collected to determine compliance with groundwater standards in Title 15A, North Carolina Administrative Code, Subchapter 2L (15A NCAC 2L). It also addresses treatment of groundwater quality samples for metal analyses and is applicable as follows:

> 15A NCAC 2L .0202(g), which addresses Class GA Standards for groundwater, states … "the standard refers to the total concentration in micrograms per liter of any constituent in a dissolved, colloidal or particulate form which is mobile in groundwater."

The purpose of collecting and analyzing groundwater samples is to obtain a representation of constituents that are mobile in groundwater. This can usually be achieved with few problems when clear samples are collected from wells that have been properly constructed and developed so that sediment in the water is minimal. However, for those samples that are not clear, it is difficult to differentiate between sediment that represents formational material versus mobile particulates or precipitates. Recently established EPA and USGS metals sampling protocols requiring turbidity level measurements have provided some additional guidance regarding this distinction. Well water samples that are highly turbid on a continuous basis may be a result of improper well construction. Therefore, it should be noted that the sampling procedures in this policy are not intended to be used in lieu of proper well construction standards found in 15A NCAC 02C .0100.

METHODOLOGY

Sample preparation for metals analysis by Standard Method 3030C for compliance with groundwater standards in 15A NCAC 2L will no longer be required. The basic preparation requirements of 3030C for determination of total metal concentrations in unfiltered samples are already incorporated and addressed in current methods from sources listed in 15A NCAC 2L .0112. Those sources include 40 CFR Part 136, which addresses approved methods under the Clean Water Act.

AQUIFER PROTECTION SECTION
1636 Mail Service Center, Raleigh, North Carolina 27699-1636
Location: 512 N. Salisbury St. Raleigh, North Carolina 27604
Phone: 919-807-6464 \ FAX: 919-807-6480\FAX: 919-807-6496
Internet: www.ncwaterquality.org

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In order to ensure that any required analysis reflects as little bias as possible due to the presence of sediment in samples being analyzed for metals that are mobile (i.e. dissolved and colloidal phases), the following sample collection protocols, based on EPA/USGS guidance, are required:

1. Redevelop wells, if necessary, to ensure turbidity levels are <10 NTU or until turbidity levels are stable. Turbidity is considered stable when three consecutive measurements vary no more than 10%.

   Turbidity measured in the field using a portable meter is not currently defined by certification rules as a field parameter. Field turbidity measurements are used to determine adequate purging and are not reported for permit compliance; therefore, certification is not required. Collectors must, however, follow equipment manufacturers' approved procedures for turbidity measurements when using portable meters in the field for purging during sample collection.

2. Use specific groundwater sample collection techniques such as low flow/low stress purging and sampling using an adjustable rate pump to minimize turbidity. Use the same pump for purging and sampling without removing it from the well. Purge wells before sampling to ensure turbidity levels are <10 NTU, or vary no more than 10%, and other field parameter measurements are stable. If the turbidity level is >10 NTU and has not stabilized within five well volumes, but is within +/- 5 NTU between measurements and decreasing, additional purging should be considered. It is at the discretion of the sample collector, however, whether or not to collect a sample or to continue purging to collect the best sample possible. Report the turbidity level with other field parameters for each sampling event.

3. Collect unfiltered samples acidified with 5 mL of concentrated nitric acid per liter of sample (more if necessary) to achieve a pH < 2 at the time of collection. Acid may be added to the samples in the field at the time of collection or may be added to the clean containers prior to transport to the field. Samples must be acidified at least 24 hours prior to analysis, and have a hold time of six months in accordance with preservation requirements specified in 40 CFR Part 136. The following exception is allowed:

   In accordance with 40 CFR Part 136.3, an aqueous sample may be collected and shipped without acid preservation. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid immediately.

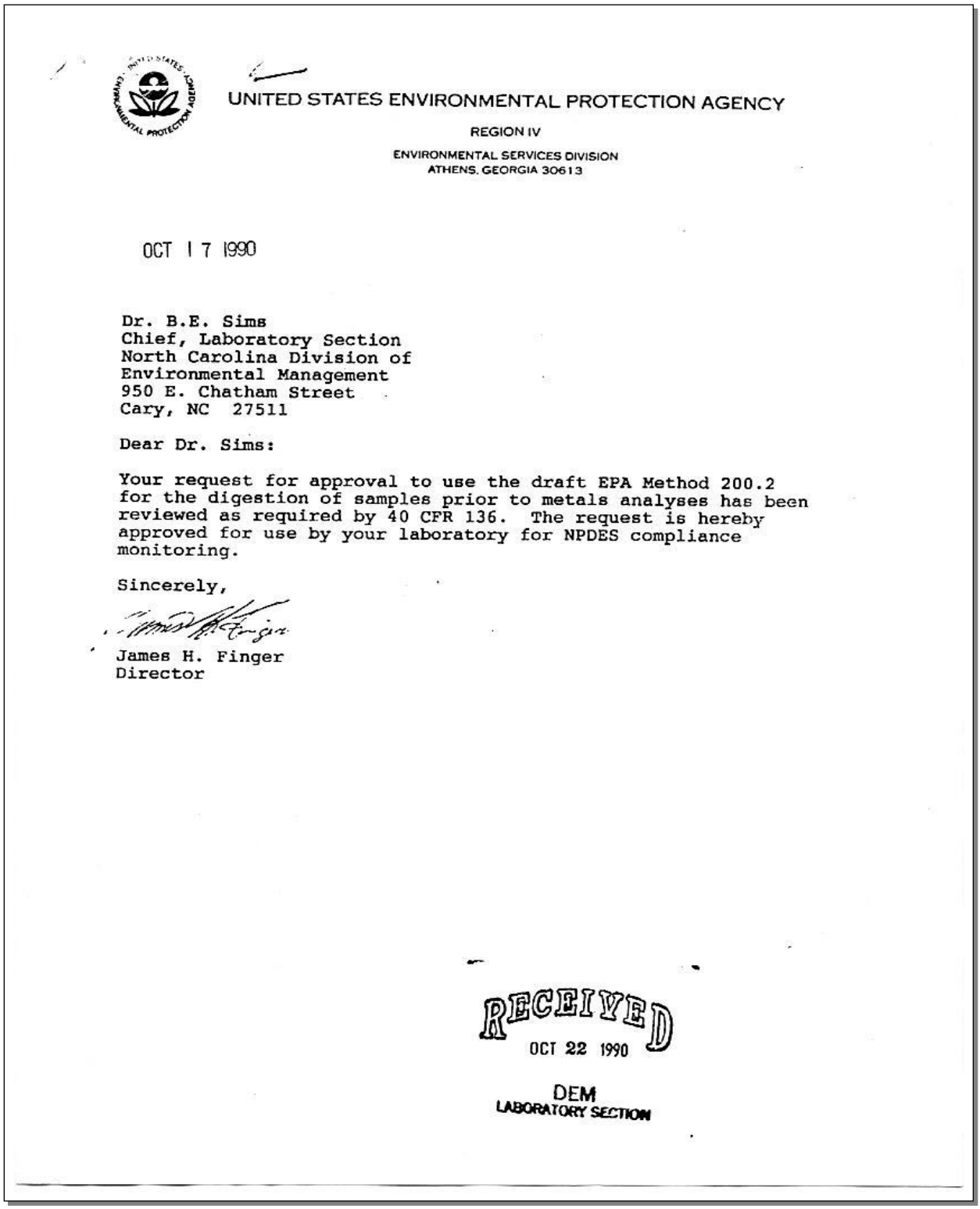
   Samples collected for mercury analysis and any other sampling requirements must be based on the requirements specified in 40 CFR Part 136 and the sample submission protocols of the Division of Water Quality (DWQ) certified laboratory analyzing the samples.

Samples must be prepared and analyzed by a laboratory certified by the DWQ using methods from sources listed in 15A NCAC 2L .0112. Water supply well samples with turbidity <1 NTU are excluded from preliminary laboratory preparation procedures as indicated in the sources listed in 15A NCAC 2L .0112.

For further information or questions, please contact staff at (919) 807-6464 in the Central Office.

cc: Kent Wiggins – DWQ Laboratory Section
Dana Satterwhite – DWQ Laboratory Certification
Roy Byrd – DWQ Laboratory Section
Grover Nicholson – Division of Waste Management, Underground Storage Tank Section
Betty Wilcox
Files

Figure 8.3. EPA Region 4 approval to use EPA Method 200.2.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IV
ENVIRONMENTAL SERVICES DIVISION
ATHENS, GEORGIA 30613

OCT 17 1990

Dr. B.E. Sims
Chief, Laboratory Section
North Carolina Division of
Environmental Management
950 E. Chatham Street
Cary, NC 27511

Dear Dr. Sims:

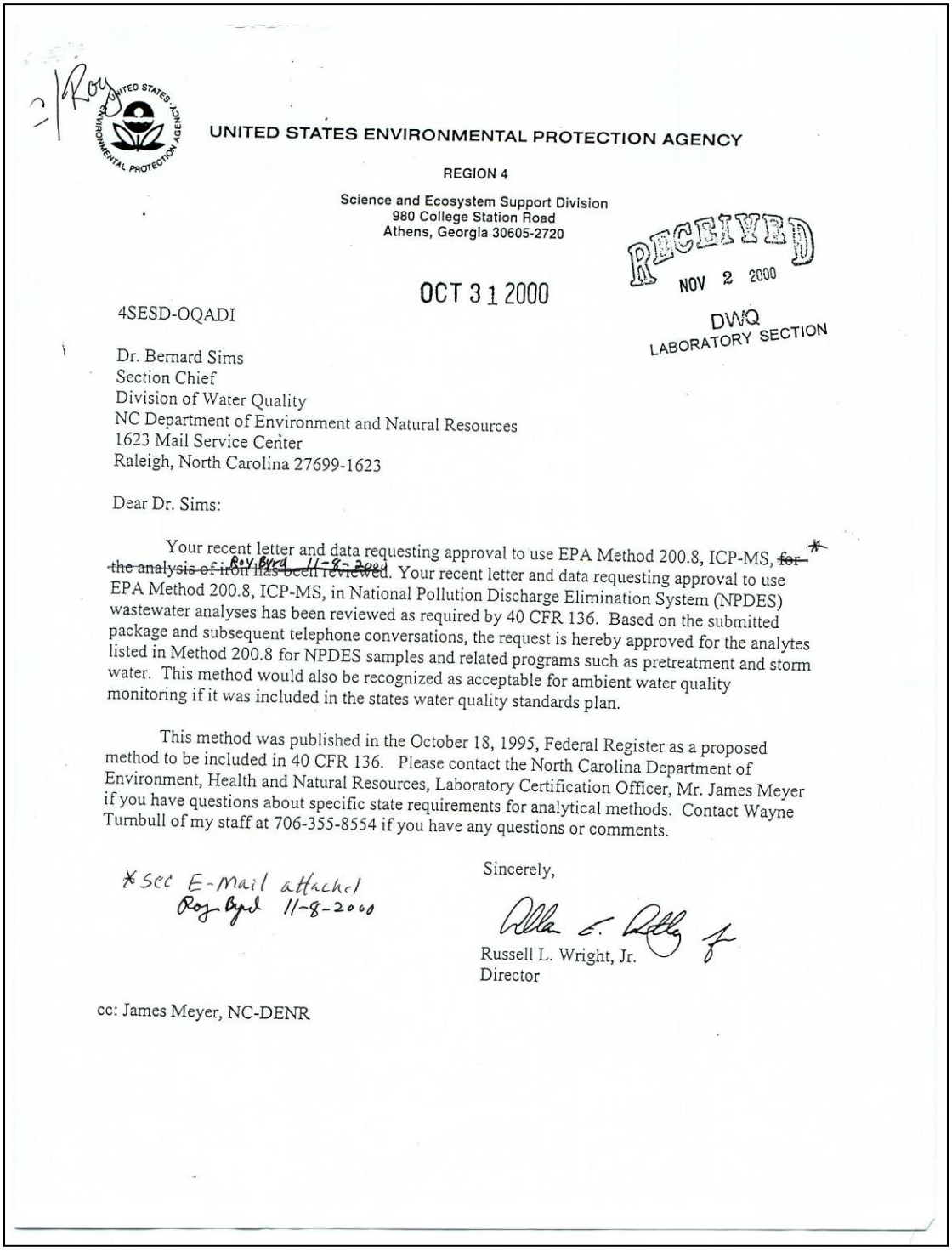
Your request for approval to use the draft EPA Method 200.2 for the digestion of samples prior to metals analyses has been reviewed as required by 40 CFR 136. The request is hereby approved for use by your laboratory for NPDES compliance monitoring.

Sincerely,

James H. Finger
Director

RECEIVED
OCT 22 1990
DEM
LABORATORY SECTION

Figure 8.4. EPA Region 4 approval for EPA Method 200.8.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 4

Science and Ecosystem Support Division
980 College Station Road
Athens, Georgia 30605-2720

RECEIVED
NOV 2 2000
DWQ
LABORATORY SECTION

OCT 31 2000

4SESD-OQADI

Dr. Bernard Sims
Section Chief
Division of Water Quality
NC Department of Environment and Natural Resources
1623 Mail Service Center
Raleigh, North Carolina 27699-1623

Dear Dr. Sims:

Your recent letter and data requesting approval to use EPA Method 200.8, ICP-MS, ~~for the analysis of iron has been reviewed~~. Your recent letter and data requesting approval to use EPA Method 200.8, ICP-MS, in National Pollution Discharge Elimination System (NPDES) wastewater analyses has been reviewed as required by 40 CFR 136. Based on the submitted package and subsequent telephone conversations, the request is hereby approved for the analytes listed in Method 200.8 for NPDES samples and related programs such as pretreatment and storm water. This method would also be recognized as acceptable for ambient water quality monitoring if it was included in the states water quality standards plan.

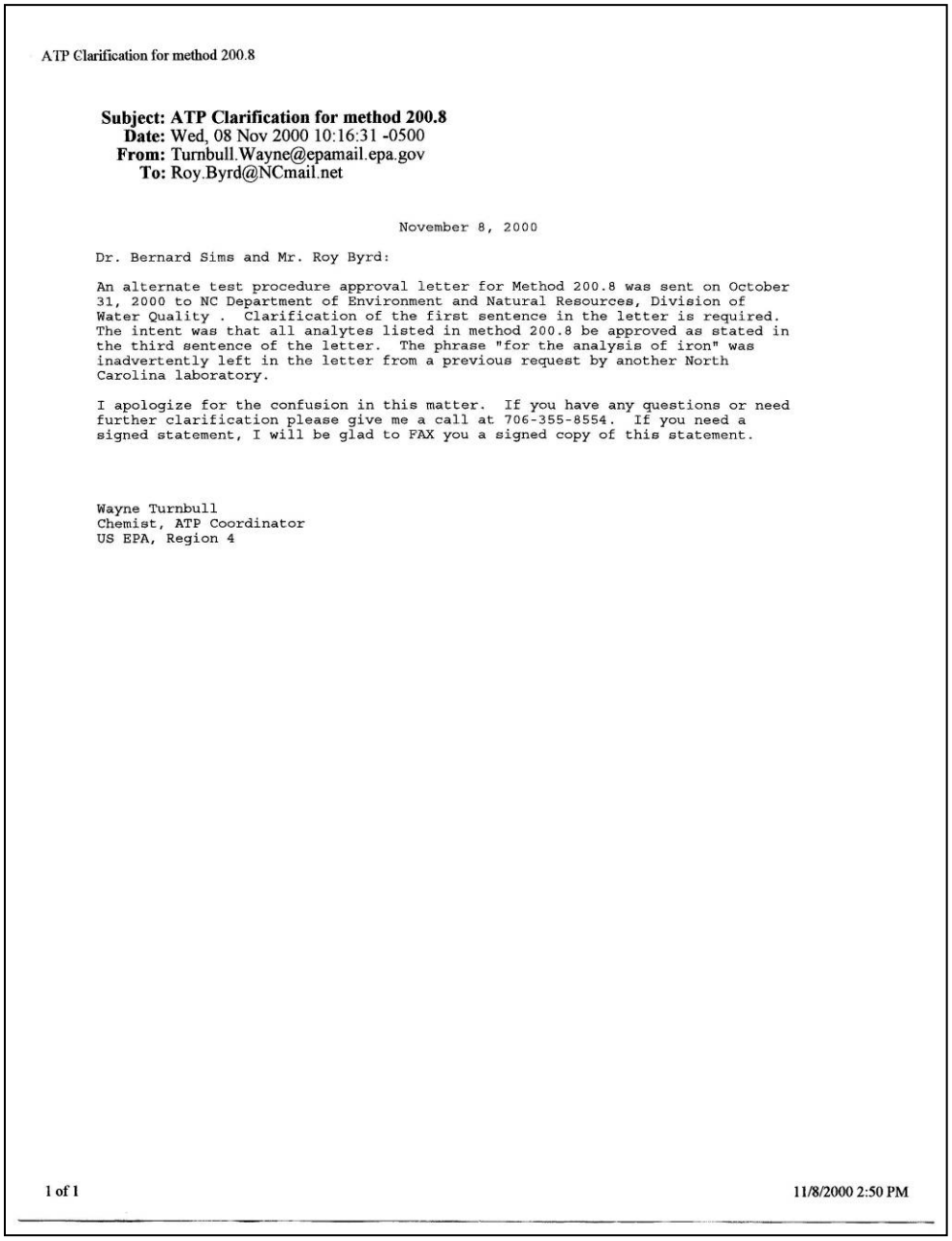
This method was published in the October 18, 1995, Federal Register as a proposed method to be included in 40 CFR 136. Please contact the North Carolina Department of Environment, Health and Natural Resources, Laboratory Certification Officer, Mr. James Meyer if you have questions about specific state requirements for analytical methods. Contact Wayne Turnbull of my staff at 706-355-8554 if you have any questions or comments.

Sincerely,

Russell L. Wright, Jr.
Director

cc: James Meyer, NC-DENR

Figure 8.5. Electronic mail clarification from EPA Region 4 regarding 200.8 approval.



ATP Clarification for method 200.8

Subject: ATP Clarification for method 200.8
Date: Wed, 08 Nov 2000 10:16:31 -0500
From: Turnbull.Wayne@epamail.epa.gov
To: Roy.Byrd@NCmail.net

November 8, 2000

Dr. Bernard Sims and Mr. Roy Byrd:

An alternate test procedure approval letter for Method 200.8 was sent on October 31, 2000 to NC Department of Environment and Natural Resources, Division of Water Quality . Clarification of the first sentence in the letter is required. The intent was that all analytes listed in method 200.8 be approved as stated in the third sentence of the letter. The phrase "for the analysis of iron" was inadvertently left in the letter from a previous request by another North Carolina laboratory.

I apologize for the confusion in this matter. If you have any questions or need further clarification please give me a call at 706-355-8554. If you need a signed statement, I will be glad to FAX you a signed copy of this statement.

Wayne Turnbull
Chemist, ATP Coordinator
US EPA, Region 4

1 of 1 11/8/2000 2:50 PM

Figure 8.6. EPA Region 4 approval for EPA Method 200.9.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 4

Science and Ecosystem Support Division
980 College Station Road
Athens, Georgia 30605-2720

NOV 16 2001

RECEIVED
NOV 19 2001
DWQ
LABORATORY SECTION

4SESD-OQADI

Mr. Steve Tedder
Section Chief
Division of Water Quality
North Carolina Department of Environmental Resources
1623 Mail Service Center
Raleigh, North Carolina 27699-1623

Dear Mr. Tedder:

Your request for approval to use EPA Method 200.9 for the analyses of lead, arsenic, selenium, cadmium, copper, nickel, and silver in waste water has been reviewed as required by 40 CFR 136. The request is hereby approved to use Method 200.9 for analyzing the metals listed above provided all quality assurance criteria are met for the method. To analyze additional metals using 200.9, please submit the supporting documentation for the additional metals. Because of the sensitivity of the methodology, the quality control criteria must be closely monitored to help assure acceptable data quality. This approval covers National Pollutant Discharge Elimination System (NPDES) discharges, storm water discharges and pre-treatment discharges to publicly owned treatment works. Other types of water monitoring, including stream samples, groundwater samples and any other type of monitoring used to meet state water quality standards, must be approved by individual states in their water quality plans (standards). EPA Region 4 recognizes Method 200.9 as an appropriate procedure for analyzing samples related to state water quality monitoring.

For your information, this method was published in the October 18, 1995, Federal Register as a proposed method to be included in 40 CFR 136. We anticipate this method being promulgated in the Federal Register in the future. If you have any questions or need additional clarification, please call Wayne Turnbull of my staff at 706-355-8554.

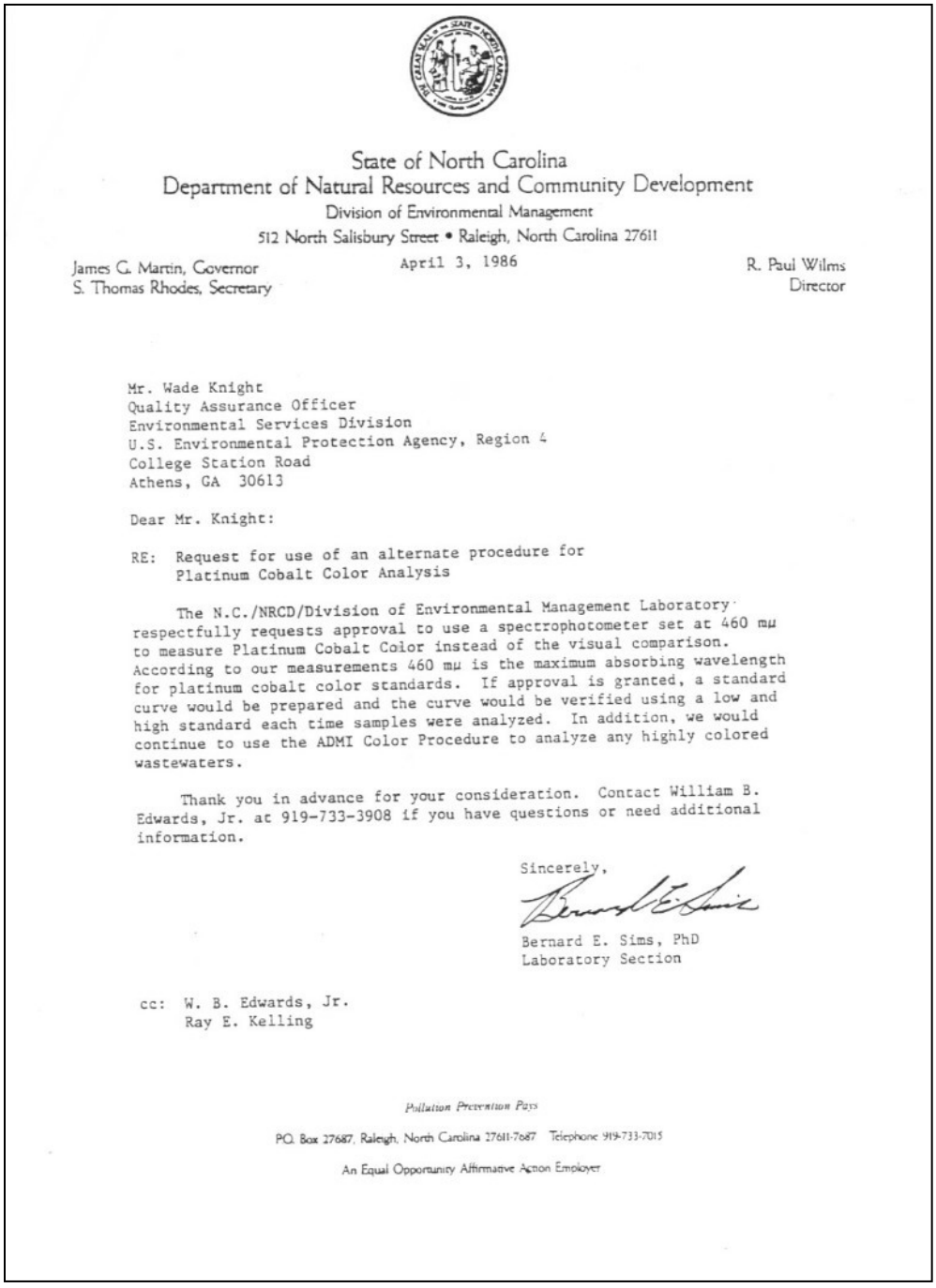
Sincerely,

Jerry Burnett /for

Allan E. Antley
Acting Director

cc: Mr. James Meyer, NC DEHNR

Figure 8.7. EPA Region 4 alternate procedure request for spectrophotometric determination of Platinum Cobalt color.



State of North Carolina
Department of Natural Resources and Community Development
Division of Environmental Management
512 North Salisbury Street • Raleigh, North Carolina 27611

James G. Martin, Governor
S. Thomas Rhodes, Secretary

April 3, 1986

R. Paul Wilms
Director

Mr. Wade Knight
Quality Assurance Officer
Environmental Services Division
U.S. Environmental Protection Agency, Region 4
College Station Road
Athens, GA 30613

Dear Mr. Knight:

RE: Request for use of an alternate procedure for
Platinum Cobalt Color Analysis

The N.C./NRCD/Division of Environmental Management Laboratory respectfully requests approval to use a spectrophotometer set at 460 mμ to measure Platinum Cobalt Color instead of the visual comparison. According to our measurements 460 mμ is the maximum absorbing wavelength for platinum cobalt color standards. If approval is granted, a standard curve would be prepared and the curve would be verified using a low and high standard each time samples were analyzed. In addition, we would continue to use the ADMI Color Procedure to analyze any highly colored wastewaters.

Thank you in advance for your consideration. Contact William B. Edwards, Jr. at 919-733-3908 if you have questions or need additional information.

Sincerely,

Bernard E. Sims, PhD
Laboratory Section

cc: W. B. Edwards, Jr.
Ray E. Kelling

Pollution Prevention Pays

P.O. Box 27687, Raleigh, North Carolina 27611-7687 Telephone 919-733-7015

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Figure 8.8. EPA Region 4 approval for spectrophotometric determination of Platinum Cobalt Color

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION IV

ENVIRONMENTAL SERVICES DIVISION
ATHENS, GEORGIA 30613

REF: 4ES/AS

May 5, 1986

Dr. Bernard E. Sims
Laboratory Section
NC Division of Environmental Management
P O Box 27687
Raliegh, NC 27611-7687

Dear Dr. Sims:

Your request to use a spectrophotometer instead of visual comparison to measure Platinum Cobalt Color in wastewater and water quality samples has been reviewed. In my opinion, use of a spectrophotometer would not be considered an alternate test procedure. This opinion is shared by Mr. Terry Covert, Chief, Equivalency Staff, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Sincerely yours,

Wade Knight

Wade Knight, Chief
Laboratory Evaluation & QA Section

9.0 Calibration Procedures and Frequency

The NC DWR laboratories are equipped with state-of-the-art instrumentation. Laboratory personnel routinely calibrate all instruments and equipment used within the Water Sciences Section Chemistry Laboratory. Some instruments or measurement devices are also annually calibrated by an external calibration service following ISO Guide 25 protocol. A summary of calibration procedures for individual instruments and tests is provided in this section. This information is summarized in Table 9-1, *Calibration Frequency, Procedures, Standards, and Acceptance Criteria for Support Equipment* and Table 9-2, *Calibration Frequency, Procedures, Standards, and Acceptance Criteria for Operational Equipment*. These tables are located at the end of Section 9.0. It is the laboratory's policy that method calibration requirements will be followed if more stringent than those described in these sections. Calibration and continuing instrument calibration verification procedures are described in detail in the laboratory SOPs.

9.1 Standards Receipt, Preparation and Traceability

Standards are purchased from commercial sources in stock solutions or mixes designed for the specific methods or as neat analytes. Certificates of analysis are shipped with each standard material by the vendor. When possible, standards are certified to meet or exceed the criteria established by the US EPA or are traceable to NIST standards.

Standards traceability logbooks are maintained by all analytical units in the Section to track the receipt, preparation, and disposition of all standard materials. A unique laboratory identification number is assigned to each standard material. The standard material is labeled with this number, which is then documented in the standard traceability logbook along with the date of preparation, date of receipt, a descriptive name of the standard, initials of the analyst, concentration (or purity), expiration date, and solvent (when applicable). If required, a standard preparation narrative is also provided in this logbook to document the preparation steps for each stock standard. The unique laboratory identification number is recorded on all appropriate data sets.

9.1.1 Analytical standard verification

Accuracy of calibration standards is verified by analyzing independently prepared standards against calibration curves produced using the calibration standards. These initial calibration verification standards are prepared using materials that are from a different source than those used for the initial calibration standards. It is acceptable to use standards from the same manufacturer as used for the initial calibration standards, as long as the primary standards used for the purchased solution can be shown to be from a different source (i.e., lot number). However, the preferred approach is to use standards from a different supplier altogether.

9.1.2 Standard preparation

Calibration standards are prepared using the procedures indicated in the *Reagents and Chemicals* section (section 7.0) of the determinative method SOP. However, general procedures are described below.

- For each analyte and surrogate (when applicable) of interest, prepare calibration standards at the minimum number of concentrations as summarized in Tables 9-1 and 9-2. If a reference or mandated method does not specify the number of calibration standards, the minimum number is 3, not including blanks. Organic curves do not include blanks.
- The lowest concentration calibration standard that is analyzed during an initial calibration is generally equivalent to the practical quantitation limit and based on the final volume of extract (or sample) described in the appropriate sample preparation SOP. In some cases, the lowest concentration standard may be less than the practical quantitation limit, but a standard is analyzed at the practical quantitation limit concentration either as part of the curve or as a daily check standard (e.g., metals). In all cases, the reporting level will be within the range of the calibration curve.
- The other concentrations define the working range of the instrument/method or correspond to the expected range of concentration found in actual samples that are also within the working range of the instrument/method. Results of samples not bracketed by initial instrument calibration standards (i.e., not within calibration range) must be reanalyzed and diluted to fall within the calibration range or be reported as having less certainty by means of defined qualifiers or case narratives. The

exception is ICP methods or other methods where the referenced method does not specify two or more standards and the instrument's linear dynamic range has been determined.

- Given the number of target compounds addressed by some of the organic methods, it may be necessary to prepare several sets of calibration standards, each set consisting of the appropriate number of solutions at different concentrations. The initial calibration will then involve the analysis of each of these sets of the appropriate number of standards.
- All initial calibrations are verified with a standard obtained from a second source and traceable to a national standard when available.
- Spiking solutions are prepared according to method specifications. If no specifications are provided, they are prepared at a concentration near the middle of the calibration range such that the spiking volume is not excessive. If the unspiked sample result is in the top 40% of the calibration range, the sample should be diluted and the spike prepared using the diluted sample. The volume of spike solution used must in all cases be ≤ 5% of the total spiked sample volume so as not to change the sample matrix significantly with spiking solution. It is preferable that the spike solution constitutes ≤1% of the total spiked sample volume so that the spiked sample can be considered a whole volume sample with no adjustment by calculation necessary. When the spike solution volume constitutes >1% of the total spiked sample volume, the sample concentration or spike concentration must be adjusted by calculation per method.

9.2 Laboratory Instrument Calibration

Calibration requirements are divided into two parts: requirements for analytical support equipment and requirements for operational instrument calibration.

9.2.1 Analytical Support Equipment Calibration

This section applies to all devices that may not be the actual test instrument, but are necessary to support laboratory operations. These include, but are not limited to, balances, ovens, refrigerators, freezers, incubators, water baths, autoclaves, temperature measuring devices, and volumetric dispensing devices if quantitative results are dependent on their accuracy (as in standard preparation and dispensing or dilution into a specified volume). Support equipment requiring calibration checks can be found in Table 9-1.

Table 9-1 also includes calibration check frequency and acceptance limits. Records of these calibration checks must be documented and include (when applicable):

- Instrument model number or specific lab identification.
- Identification of standards used for the calibration check.
- Performance tolerances.
- Results of the calibration checks, the initials of the individual making the check, and the date of the check.
- A reference for the procedure used to perform the calibration check.

9.2.2 Operational Instrument Calibration

The frequency and acceptance criteria of instrument calibration and standardization are summarized in Table 9-2. Method specific SOPs expand on the following general discussion.

9.3 General Calibration Procedures

Instrument calibration and reagent standardization for the analyses performed in the lab are in accordance with the procedures specified in the referenced method (see Section 5).

9.3.1 Calibration Documentation

All calibration records including raw data, response factors, standard concentrations, curves, reduced data, and instrument settings or conditions are stored and archived as hard or electronic copy according to laboratory standard operating procedures. Current chromatograms, curves, and results transcribed onto

forms are kept at the analysts' work areas and periodically archived into a data storage area. Initial and continuing calibrations are sorted by date for ease of location. All standard assigned unique identification numbers appear on graphs, plots, chromatograms, or curves for traceability purposes.

9.3.2 Protocol for Determining the Test Method Range of Applicability

During the development of new test methods and during initial demonstrations of capability (method validation studies), a cursory evaluation will be made of the dynamic range over which the method is applicable. That evaluation will take into consideration the type of calibration protocol (linear, nonlinear), the change in sensitivity over the tested calibration region, the detection limit of the method and the practical quantitation limit. Once a valid range of applicability is established, calibration standards will be used to bracket the range of quantitation. Results reported from data that were generated outside the determined range of applicability will be flagged as estimates (unless the sample was diluted prior to analysis in order to bring concentrations within the established test method range of applicability).

During the establishment of the test method range of applicability, calibration standards will be prepared and analyzed over the estimated or published range of applicability. For inorganic parameters, if a linear calibration protocol is to be used, the correlation coefficient of the calibration values plotted against their respective responses (absorbance, concentration, etc.), must be greater than or equal to 0.995. For organic parameters, if a linear calibration protocol is to be used, either a) the correlation coefficient of the calibration values plotted against their respective response factors must be greater than or equal to 0.99, b) the relative response factors (response factor/calibration value) over the range of calibration must meet the relative standard deviation criterion of the applied method or c) other conditions for linearity specified in the applied, published method must be met.

If the above conditions are not met, either the linear dynamic range must be decreased until those conditions are met or, in some cases, a non-linear calibration protocol may be used. Whenever a non-linear calibration protocol is utilized, a minimum of 5 calibration points must be defined for a second order fit; a third order fit requires a minimum of 6 calibration points. When using non-linear calibration procedures, loss in sensitivity (Δ response/Δ concentration) can occur at high concentrations. To ensure that signals are not quantified in regions of poor sensitivity, control standards must be analyzed at the highest point of the nonlinear calibration curve during method validation and must meet the reference method acceptance criteria for calibration.

The lower limit of the test method range of applicability is normally established at the practical quantitation limit. The initial demonstration of capability includes establishment of the method detection limit and practical quantitation limit which is generally set at three to five times the calculated method detection limit.

9.3.3 General GC Calibration Procedures

General calibration procedures are described below for GC procedures using non-Mass Spectrometer (MS) detection. The calibration procedures for other techniques are described within the applicable method SOP.

9.3.3.1 External Standard Calibration Procedure

External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. Sample peak areas (or peak heights) are compared to peak areas (or peak heights) of the standards. The ratio of the detector response to the amount (mass) of analyte in the calibration standard is defined as the calibration factor (CF).

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

For multi-component analytes, see the appropriate method SOP for information on calibration.

The CF can also be calculated using the concentration of the standard rather than the mass in the denominator of the equation above. However, the use of concentrations in CFs will require changes to the equations that are used to calculate sample concentrations.

Some analytical systems use software programs that perform these calculations automatically. These programs should be checked periodically by manual calculation comparison to test for accuracy.

9.3.3.2 Internal Standard Calibration Procedure

Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample or sample extract prior to injection. The ratio of the peak area (or peak height) of the target compound in the sample or sample extract to the peak area (or peak height) of the internal standard in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), and may also be known as a relative response factor in other methods.

In many cases, internal standards are recommended. These recommended internal standards are often brominated, fluorinated, or stable isotopically labeled analogs of specific target compounds, or are closely related compounds whose presence in environmental samples is highly unlikely. If internal standards are not recommended in the method, then the analyst needs to select one or more internal standards that are similar in analytical behavior to the compounds of interest, and not expected to be found in the sample otherwise. The use of specific internal standards is available in the method SOP.

Whichever internal standards are employed, the analyst needs to demonstrate that the measurement of the internal standard is not affected by method analytes and surrogates or by matrix interferences. In general, internal standard calibration is not as useful for GC methods with non-MS detectors because of the inability to chromatographically resolve many internal standards from the target compounds. The use of MS detectors makes internal standard calibration practical because the masses of the internal standards can be resolved from those of the target compounds even when chromatographic resolution cannot be achieved.

When preparing calibration standards for use with internal standard calibration, add the same amount of the internal standard solution to each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards, whereas the concentrations of the target analytes will vary. The internal standard solution will contain one or more internal standards and the concentration of the individual internal standards may differ within the spiking solution (e.g., not all internal standards need to be at the same concentration in this solution). The mass of each internal standard added to each sample extract immediately prior to injection into the instrument or to each sample prior to purging must be the same as the mass of the internal standard in each calibration standard. The volume of the solution spiked into sample extracts should be such that minimal dilution of the extract occurs (e.g., 10 µL of solution added to a 1 mL final extract results in only a negligible 1% change in the final extract volume which can be ignored in the calculations).

An ideal internal standard concentration would yield a response factor of 1 for each analyte. However, this is not practical when dealing with more than a few target analytes. Therefore, as a general rule, the amount of internal standard should produce an instrument response (e.g., area counts) that is no more than 100 times that produced by the lowest concentration of the least responsive target analyte associated with the internal standard. This should result in a minimum response factor of approximately 0.01 for the least responsive target compound.

For each of the initial calibration standards, calculate the RF values for each target compound relative to one of the internal standards as follows:

$$RF = \frac{A(s) * C(is)}{A(is) * C(s)}$$

Where:
A(s) = Peak area (or height) of the analyte or surrogate
A(is) = Peak area (or height) of the internal standard
C(s) = Concentration of the analyte or surrogate, in µg/L
C(is) = Concentration of the internal standard, in µg/L

Note that in the equation above, RF is unitless, i.e., the units from the two area terms and the two concentration terms cancel out. Therefore, units other than µg/L may be used for the concentrations of the analyte, surrogate, and internal standard, provided that both C(s) and C(is) are expressed in the same units. The mass of the analyte and internal standard may also be used in calculating the RF value.

9.3.3.3 Evaluating the Linearity of the Initial Calibration

To evaluate the linearity of the initial calibration, calculate the mean CF (external standard calibration) or RF (internal standard calibration), the standard deviation (SD) and the RSD as follows:

$$Mean\ CF = \overline{CF} = \frac{\sum_{i=1}^{n}(CF(i))}{n}$$

$$Mean\ RF = \overline{RF} = \frac{\sum_{i=1}^{n}(RF(i))}{n}$$

The variance and standard deviation of a data set measures the spread of the data about the mean of the data set.

The variance of a sample of size *n* represented by s^2 is given by:

$$s^2 = \frac{\sum(X-\bar{X})^2}{n-1}$$

The standard deviation (SD) can be calculated by taking the square root of the variance.

$$SD = \sqrt{\frac{\sum(X-\bar{X})^2}{n-1}}$$

If the RSD of the calibration or response factors is less than or equal to the acceptance limit stated in Table 9-2 over the calibration range, then linearity through the origin may be assumed, and the average calibration response factor may be used to determine sample concentrations.

$$RSD = \left(\frac{SD}{mean\ CF}\right) x\ 100$$

$$RSD = \left(\frac{SD}{mean\ RF}\right) x\ 100$$

9.3.4 Percent RSD Corrective Action

Given the potentially large numbers of analytes that may be analyzed in some methods, it is likely that some analytes may exceed the acceptance limit for the RSD for a given calibration. In those instances, the following steps are recommended, but not required.

- The first step is generally to check the instrument operating conditions. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

- If the RSD for any analyte is greater than the applicable acceptance criteria in Table 9-2, the analyst may wish to review the results (area counts, calibration or response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

- A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. Note: Changes to the upper end of the calibration range will affect the need to dilute sample above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

NOTE: As noted in Section 9.3.2, the practical quantitation limit is equal to the concentration of the lowest standard analyzed during the initial calibration. Hence, narrowing the calibration range by changing the concentration of the lowest standard will change the practical quantitation limit. When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the laboratory must ensure that the practical quantitation limit is at least as low as the regulatory limit or action level.

In those instances where the RSD for one or more analytes exceeds the acceptance criteria, the initial calibration may still be acceptable if the following conditions are met:

- The mean of the RSD values for all analytes in the calibration is less than or equal to the acceptance criteria. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes. If no analyte has an RSD above the acceptance criteria, then the mean RSD calculation need not be performed.

- The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific sample. In other words, if the target analyte is part of the calibration standard, its RSD value is included in the evaluation.

- The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded the acceptance criteria and the results of the mean RSD calculation.

  NOTE: The analyst and the data user should be aware that the mean RSD approach described above will lead to greater uncertainty for those analytes for which the RSD is greater than the acceptance criteria. The analyst and the data user should review the associated quality control results carefully, with particular attention to the matrix spike and the laboratory control sample results, to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to employ another calibration approach or adjust the instrument operating conditions or the calibration range until the RSD meets the acceptance criteria.

- If all of the conditions above are met, then the average calibration or response factor may be used to determine sample concentrations.

Use of other types of calibration (i.e., linear calibration using a least squares regression or non-linear calibration) may be described in manufacturer's manuals or within a published method. These procedures must be reviewed, incorporated into the appropriate SOP and approved by the QA/QC Coordinator prior to their use.

9.3.5 Retention Time Windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC methods that do not employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives or may cause unnecessary reanalysis of sample when surrogates or spiked compounds are not identified or are erroneously identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

The following subsection describes the approach used to establish retention time windows for GC methods. Note: The criteria listed in this section are provided for GC procedures using non-MS detection. Identification procedures are different for GC/MS and are detailed in the analytical SOPs.

Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72-hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks (see the determinative methods for more details) and calculate the mean and standard deviation of those peaks.

If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).

The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as +/- 3 times the standard deviation of the mean absolute retention time established during the 72 hour period. If the default standard deviation in the above example is employed, the width of the window will be 0.03 minutes.

Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

The laboratory must calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed or more frequently as detailed in the analytical SOP.

If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose a window that minimizes false negatives and positives and apply it to all compounds. As noted above, other approaches may also be employed, but must be documented by the analyst. In general, you should not use a window greater than 0.2 to 0.3 minutes. If windows larger than this have been determined a cause should be looked for and the windows should be re-determined.

The surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

9.3.6 Calibration Verification

The calibration relationship established during the initial calibration must be verified at periodic intervals as specified in Table 9-2. The process of calibration verification applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models.

NOTE: The process of calibration verification referred to here is fundamentally different from the approach called "calibration" in some methods. As described in those methods, the calibration factors or response factors calculated during calibration are used to update the calibration factors or response factors used for sample quantitation. This approach amounts to a daily single-point calibration, and is neither appropriate nor permitted in SW-846 chromatographic procedures for trace environmental analyses.

As a general rule, the initial calibration must be verified at the beginning of each 12-hour analytical shift during which samples are analyzed. Some methods may specify more or less frequent verifications in which case the stricter frequency will be used. The 12-hour analytical shift begins with the injection of the calibration verification standard (or the MS tuning standard in MS methods). The shift ends after the completion of the analysis of the last sample or standard that can be injected within 12 hours of the beginning of the shift. Continuing instrument calibration verification must be repeated at the beginning and end of each analytical batch for non-GC/MS methods. The concentration of the calibration verification shall be varied within the established calibration range. If an internal standard is used, i.e., GC/MS, only one continuing calibration verification must be analyzed per analytical batch.

If the response (or calculated concentration) for an analyte is within the acceptance limits of the response obtained during the initial calibration, then the initial calibration is considered still valid and the analyst may continue to use the CF or RF values from the initial calibration to quantitate sample results. If the response (or calculated concentration) for any analyte varies from the mean response obtained during the initial calibration by more than the acceptance criteria, then the initial calibration relationship may no longer be valid. If routine corrective action procedures fail to produce a second consecutive (immediate) calibration verification within acceptance criteria, then either the laboratory has to demonstrate performance after corrective action with two consecutive successful calibration verifications, or a new initial instrument calibration must be performed. However, sample data associated with an unacceptable calibration verification may be reported under the following special conditions:

1. When the acceptance criteria for the calibration verification are exceeded high, i.e., high bias, and there are associated samples that are detects, then those detects may be reported with qualification. Associated samples that are non-detects do not need qualifying. The detect samples affected by the unacceptable calibration verification may be reanalyzed after a new calibration curve has been established, evaluated and accepted.
2. When the acceptance criteria for the calibration verification are exceeded low, i.e., low bias, those sample results may be reported with qualification if the sample results exceed a maximum regulatory limit/decision level. Otherwise, the samples affected by the unacceptable verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted. Those multi component analyses with calibration verification exceeded low, i.e., low bias, may result in qualification of non-detect samples as well as detect samples with the appropriate data qualifier spelled out in analytical SOP or validation document.

In keeping with the approach described for initial calibration, if the average of the responses for all analytes are within that required in Table 9-2, then the calibration has been verified. However, the conditions in Section 9.3.6 also apply. The average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project. The effect of using the average of the response for all analytes for calibration verification will be similar to that for the initial calibration - namely, that the quantitative results for those analytes where the difference is greater than the limit will include a greater uncertainty. If the calibration does not meet the limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within the acceptance criteria, then a new initial calibration must be prepared unless there is an exception allowed in the analytical method or SOP.

9.3.7 Verification of Linear Calibrations

Calibration verification for linear calibrations involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the procedure specified in the method SOP.

$$\% \text{ Drift} = \frac{\text{Calculated concentration - Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

Where the calculated concentration is determined using the mean calibration factor or response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared, use

$$\% \, Difference = \frac{CF(V) - MeanCF}{CF} * 100 \qquad \text{or} \qquad \% \, Difference = \frac{RF(V) - MeanRF}{RF} * 100$$

Where CF(v) and RF(v) are the calibration factor and the response factor (whichever applies) from the analysis of the verification standard, and CF and RF are the mean calibration factor and mean response factor from the initial calibration.

Except where superseded in certain determinative methods, the %Difference or %Drift calculated for the calibration verification standard must be within +/- 15% for each analyte, or averaged across all analytes, before any sample analyses may take place.

9.3.8 Verification of Non-Linear Calibrations

Calibration verification of a non-linear calibration is performed using the percent drift calculation described in Section 9.3.7. Calibration verification must be acceptable before any sample analyses may take place. It may also be appropriate to employ two standards at different concentrations to verify the calibration. This is outlined in the method SOP when used.

Regardless of whether a linear or non-linear calibration model is used, and the percent drift difference criterion is not met, then no sample analyses may take place until the calibration has been verified or a new initial calibration is performed that meets the specifications in the method SOP. If the calibration cannot be verified after the analysis of a single verification standard, adjust the instrument operating conditions or perform instrument maintenance, and then analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, and a new initial calibration is performed.

All target analytes and surrogates, including those reported as non-detects, must be included in a periodic calibration to confirm retention time and demonstrate that calibration verification criteria are being met. The frequency of this calibration is noted in Table 9-2.

Samples analyzed using external standards must be bracketed by periodic analysis of standards that meet the QC acceptance criteria (e.g., calibration and retention time). The results from these bracketing standards must meet the calibration verification criteria and the retention time criteria. However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, and the analyte was not detected in any of the previous samples during the analytical shift, then the sample extracts do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present.

9.4 Instrument-Specific Calibration Procedures

The brief narratives describing instrument calibration procedures listed below meet or exceed cited method requirements. All calibrations are recorded in the raw data or on bench worksheets for that analytical run.

9.4.1 Support Equipment

pH meter

Each pH meter is calibrated daily with two or three standard buffers, generally at pH 4.0, 7.0 and 10.0, and checked with a third buffer at or near pH 7.0, which must indicate $\pm$0.10 pH units of its given value. Additional checks of the pH meter must be performed with buffers other than 4 or 10 if samples are outside the pH range of 4-10. Manual or automatic temperature compensation is performed, depending on the meter. The thermometer is verified with an NIST traceable thermometer. Calibration information from manual determinations is recorded in a calibration logbook for the pH meter or on laboratory bench worksheets.

Analytical Balance

Electronic analytical balances are calibrated daily or day of usage, with internal mechanisms, if available. The calibration of the balance must be checked daily or prior to usage by the analysis of an ASTM Class 1 and 2 weight that is near the approximate weight of material that is being determined. The balance must be checked quarterly by the analysis of a series of at least 3 weights that the lab routinely determines or that bracket the approximate weights of the materials being measured. The daily and quarterly calibration checks must be documented in a logbook kept with the balance or on laboratory bench worksheets. In addition, on a yearly basis, all analytical balances are calibrated, cleaned and certified by an independent company and the weights and weight sets used in the analytical units are checked against primary standard weights. The primary weights are recalibrated every 5 years.

Thermometer Calibration and Temperature Checks

Equipment such as refrigerators, freezers, ovens, waterbaths, hot blocks, and incubators are periodically checked with NIST traceable thermometers. Refrigerators and freezers are checked daily and the temperatures documented in a notebook or on laboratory bench worksheets. The temperature of microbiological incubators must be checked and recorded twice daily. Sample storage refrigerators should be set to 4°C. They must maintain a temperature less than 6°C, and must not freeze aqueous samples. All liquid-in-glass thermometers are calibrated at least annually against an NIST traceable thermometer. Digital thermometers are calibrated at least quarterly against an NIST traceable thermometer. This may be performed by an independent company. Thermometers are replaced when they are not within allowable tolerances, otherwise they are labeled and the proper correction is applied.

Mechanical Volumetric Liquid-Dispensing Devices Calibration

Mechanical volumetric liquid-dispensing devices (e.g., fixed and adjustable auto-pipettors, bottle-top dispensers, etc.) are calibrated at least twice per year, approximately six months apart. Each liquid-dispensing device must meet the manufacturer's statement of accuracy. For variable volume devices used at more than one setting, the accuracy is checked at the maximum, middle and minimum values. Testing at more than three volumes is optional. When a device, capable of variable settings, is dedicated to dispense a single specific volume, calibration may be performed at that setting only. This may be performed by an independent company.

9.4.2 Metals Calibration Protocols

ICP-AES

The Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) is calibrated with each analytical batch and whenever the response of the Continuing Calibration Verification Standard (CCVS) varies by greater than ± 10% from the initial calibration. The initial calibration curve is generated using an instrument blank and a minimum of four standards encompassing the concentration range of interest. The curve fit is linear, first order. The initial calibration curve must meet the following criteria:

- Accuracy of a daily Quality Control Check Sample (QCS) must be in the range of 90-110 %.
- Calibration/instrument blank must exhibit a response < ½PQL;
- An interference check standard is analyzed and values must agree within ± 15 % of the components' true values.

A (CCVS) at the mid-point of the calibration curve and an instrument blank are analyzed every 10 samples and at the end of the run to insure the continuing validity of the initial calibration. The CCVS must agree within ± 10 % of the initial calibration. In addition, the blank must exhibit a response < ½PQL of the analysis components.

All calibration runs and sample results to which the calibration applies are recorded on the system hard disk. All data are archived to the network, where they are stored permanently on optical disk. All records are filed by run date

ICP-AES (Optima 3000 XL) Calibration Protocol Summary.

Calibration Check	200.7 Criteria
Minimum number of calibration points	4
Initial Instrument Performance Check (IPC)	±5% of true value
Initial Calibration Blank (ICB)	<½PQL
PQL standard	Detected; ±50% of true value
Continuing Calibration Verification Standard (CCVS)	±10% of true value
Continuing Calibration Blank (CCB)	<½PQL

ICP-MS

The Inductively Coupled Plasma-Mass Spectrometer's (ICP-MS) performance is verified prior to the beginning of an analysis run and every 12 hours thereafter, using a multi-element check solution containing Ce, Ba, Pb, Mg, In and Rh at 10 ug/L each. The performance analysis must meet the following criteria:

- $Ce^{++/}$ Ce ratio is ≤ 3 %;
- CeO/Ce ratio is ≤ 2.5 %;
- Mg 4 intensity must be ≥ 20,000 ions/sec:
- In 114.9 intensity must be ≥ 50,000 ions/sec;
- Be9 intensity must be ≥3,000 ions/sec.
- U238 intensity must be ≥ 40,000 ions/sec:

The results from this optimization/tune are recorded in the instrument's daily operating log.

The ICP-MS is calibrated with each analytical batch and whenever the continuing calibration verification standard (CCVS) varies by greater than 10% from the initial calibration. The initial calibration curve is generated using an instrument blank and five standards. The curve fit is linear, first order.
Quantitations are carried out using the internal standard technique. The initial calibration curve must meet the following criteria:

- Accuracy of a daily Quality Control Check Standard (QCS) must be in the range of 85-115 %.
- Calibration/instrument blank must exhibit a response < ½PQL.

A Continuing Calibration Verification Standard (CCVS) at the mid-point of the calibration curve and an instrument blank are analyzed at least every 10 samples. The CCVS must agree within 15% of the initial calibration. In addition, the blank must exhibit a response below the MDL of the analysis components.

The internal standard acceptance criteria for natural water samples is 60-125% of the internal standard's initial intensity for the analytical run as per EPA Method 200.8. The internal standard acceptance criteria for solid and waste samples is 30-130% of the internal standard's initial intensity for the analytical run as per EPA Method 6020.

The summary data for each run is archived to memory stick and to the network, where it is stored permanently on optical disk.

NexION 350X) Calibration Protocol Summary.

Calibration Check	200.8 Criteria
Minimum number of calibration points	4
Initial Calibration Verification (ICV)	±10% of true value
Initial Calibration Blank (ICB)	<½PQL
PQL standard	Detected; ±50% of true value
Continuing Calibration Verification Standard (CCVS)	±15% of true value
Continuing Calibration Blank (CCB)	<½PQL

AA (Atomic Absorption)

Atomic absorption spectrophotometers are calibrated daily with the specified number of calibration standards, including a calibration blank. The curve fit is linear, first order. The exception to this curve fit is Cadmium (Cd) which is a non-linear through zero. The correlation coefficient of the regression curve must be greater than or equal to 0.995. An initial calibration verification standard (ICVS) is analyzed immediately upon calibration and must meet acceptance criteria. Continuing calibration verification standards (CCVS) are analyzed after every 10 samples and at the end of the sequence and must meet the acceptance criteria. An initial calibration blank (ICB) or continuing calibration blank CCB) is analyzed immediately after the verification standards and must meet the acceptance criteria.

All calibration acceptance criteria and pass/fail status are documented on raw calibration data files. Calibration data is filed by run date and method number. The sample numbers to which calibrations apply are recorded on calibration records.

GFAA (Graphite Furnace Atomic Absorption) Calibration Protocol Summary.

Calibration Check	200 series	200.9
Minimum number of calibration points	4	4
Initial Calibration Verification (ICV)	±10% of true value	+5% of true value
Initial Calibration Blank (ICB)	<½PQL	<½PQL
Continuing Calibration Verification Standard (CCVS)	±10% of true value	+10% of true value
Continuing Calibration Blank (CCB)	<½PQL	<½PQL

All sample results must be bracketed by acceptable calibration standards.

CVa (Cold Vapor Atomic Absorption - Mercury) Calibration Protocol Summary.

Calibration Check	200 series
Minimum number of calibration points	6
Initial Calibration Verification (ICV)	±5% of true value
Initial Calibration Blank (ICB)	<½PQL
Continuing Calibration Verification Standard (CCVS)	±10% of true value
Continuing Calibration Blank (CCB)	<½PQL

All sample results must be bracketed by acceptable calibration standards.

Purge and Trap Cold Vapor Atomic Florescence Spectrometry

The calibration must contain a minimum of 5 non-zero points and the results of analysis of 3 system blanks. The lowest calibration point must be at the minimum level (ML, 0.50 ng/L). Successive calibrations points must be no greater than a factor of 10 and no less than a factor of 2 and should be approximately evenly spaced on a logarithmic scale over the calibration range up to 100 ng/L. After the relative standard deviation (RSD) of the calibration factor, the percent recovery of the lowest standard, the calculated concentration of Hg in the system blanks, and the standard deviation (n-1) of the concentration of the system blanks have all met the criteria, analysis of the analytical batch may proceeded. To demonstrate lack of carryover from samples equal to the highest calibration standard at the 0.5 ng/L level, a blank must be analyzed immediately after the high standard whenever a change is made to the analytical system that may affect carryover.

If the analysis of the ongoing precision and recovery (OPR) sample at the beginning and end of the analytical batch, a quality control sample (QCS), and at least three method blanks are all within the required limits, then the results of the analysis of the may be reported. An analytical batch consists of up to 20 samples and must be bracketed by OPR analyses. Samples include only field blanks and the associated collected samples (including field duplicates) but do not include any other blanks, QCS, OPR checks, or spiked blanks and samples. Results for samples below ML are reported as 0.50U. Results above ML but below the upper calibration limit are reported to 3 significant figures.

Purge and Trap CVAFS Calibration Protocol Summary – Low Level Mercury

Calibration Check	EPA Method 1631E
Minimum number of calibration points	5, Non zero
Minimum number of system blanks	3
RSD of the calibration factor	≤ 15%
% Recovery for the lowest standard (0.5 ng/L)	75-125%,
Calculated concentration of system blanks	All must be < 0.50 ng/L
SD (n-1) of the concentration of system blanks	<0.1 ng/L
Ongoing precision and Recovery (OPR), 5 ng/L	77-123%
Quality Control Sample (QCS), must be from a source different from the solution used to produce the calibration standards, OPR, and spike solution.	Not specified. Generally, acceptance limits on Certificate of Analysis or the same criteria as the OPR.
Method Blanks	Minimum of 3 all <0.50 ng/L.

9.4.3. General Chemistry

Flow Injection Auto Analyzers

A calibration curve containing 5-8 calibration standard levels is analyzed daily, at the start of each analytical run sequence. External standard calibration is utilized. The calibration curve must meet the following criteria:

- The correlation coefficient for the linear regression must be ≥ 0.995 using a regression fit;
- Accuracy of a daily QC Check Standard must be in the range of 90-110 % or within the manufacturer's accuracy acceptance range, unless historical data indicate that tighter control limits can be routinely maintained;
- Calibration/instrument blank must exhibit a response < ½PQL.

Continuing Calibration Check Standards (CCCS) at the concentration mid-point of the initial calibration are analyzed every 10 samples, to insure the continuing validity of the initial calibration. The CCCS must agree within +/-10 % of the response of the initial calibration to be valid. If this check fails, the instrument is re-calibrated. In addition, the calibration/instrument blank, which is analyzed every 10 samples, must exhibit a response below ½PQL. Samples analyses must be bracketed by calibration verification standards that meet control criteria.

Calibration information is recorded on the computer printout of raw data. The calibration runs are also recorded on the system hard disk and stored on floppy diskette or thumb drive. All initial calibration raw data is filed by run date and method number. The sample numbers to which calibration apply are recorded on calibration records. Applicable calibration run dates are recorded on sample raw data records.

Ion Selective Electrode (ISE)

Ion selective electrodes are calibrated daily with a minimum of three standards and a blank. The calibration curve is established by linear regression applied to the standard concentrations versus the corresponding millivolt values.

The calibration curve must meet the following criteria:

- The correlation coefficient must be greater than or equal to 0.995.
- The slope for the 1 to 10 ppm standards should be -59 ± 4 mV /decade and the efficiency (of meter) should be -1.00 ±0.08 (or follow the manufacturer's guidance for acceptable operating parameters).
- Accuracy of a daily Quality Control Check Standard (QCS) must be in the range of 90-110 % or within the manufacturer's accuracy acceptance range; unless historical data indicate that tighter control limits can be routinely maintained.

Calibration/instrument blank must exhibit a response < ½PQL. A CCCS at the concentration mid-point is analyzed every 10 samples, to insure the continuing validity of the initial calibration. The CCCS must agree within ±10% of the response of the initial calibration to be valid. If this check fails, the instrument is re-calibrated. Data must be bracketed by calibration standards that meet control criteria to be acceptable. In addition, the calibration/instrument blank, which is analyzed every 20 samples, must exhibit a response < ½PQL.

Ion Selective Electrode calibration information is recorded on raw data bench worksheets.

Turbidimeter

Initial calibration is performed upon instrument startup and whenever the continuing calibration verification standard fails the acceptance criteria. Sealed standards are calibrated against formazin standards initially and then quarterly. The instrument is calibrated monthly and checked daily with one sealed standard for each range of interest and a blank. The calibration/instrument blank must exhibit a response below 0.05 NTU.

Calibration information is recorded on the laboratory bench worksheets.

Ion Chromatograph

Initial calibration is performed for every analytical run and whenever the response factor of the continuing calibration check standard varies by more than ±15 % from the latest initial calibration. A calibration curve is prepared for all target analytes (using a minimum of three standard concentration levels) with the lowest standard concentration at or below the reporting limit and the remaining standards defining the working range of the detector. Either linear regression or quadratic curve fitting is used, depending on the analyte. All quantitations are carried out using the external standard technique. The initial calibration curve must meet the following criteria:

- The correlation coefficient must be ≥ 0.995;
- Accuracy of a daily Quality Control Check Standard (QCS) must be in the range of 90-110 %, unless historical data indicate that tighter control limits can be routinely maintained;
- Calibration/instrument blank must exhibit a response < ½PQL.

Continuing Calibration Verification standards are analyzed at the concentration mid-point of the initial calibration. The CCVS is analyzed every 10 samples, to insure the continuing validity of the initial calibration. The CCVS must agree within 10 % of the response of the initial calibration to be valid. Sample analyses must be bracketed by calibration verification standards that meet the acceptance criteria. In addition, the calibration/instrument blank, which is analyzed every 10 samples, must exhibit response < ½PQL.

Calibration information is recorded on the computer printout of raw data. The calibration runs are also recorded on the system hard disk.

Ultraviolet-Visible (UV/VIS) Spectrophotometer

The spectrophotometer is calibrated with a minimum of five standards at least annually (some procedures/instruments may require daily calibration), when a new stock standard solution is prepared or when the continuing calibration verification standard varies by greater than ±10% from the initial calibration. All quantitations are carried out using the external standard technique. The initial calibration curve must meet the following criteria:

- The correlation coefficient must be ≥ 0.995 using a regression fit;
- Calibration/instrument blank must exhibit a response < ½PQL.

Continuing Calibration Verification standards at the concentration mid point of the initial calibration curve are analyzed immediately following the calibration standards (initial or continuing), after every 10 samples (or after every 3 samples for sulfate analyses), and at the end of each run. The CCV must agree within ± 10 % of the response of the initial calibration to be valid. Data must be bracketed by calibration verification standards that meet control criteria. In addition, the instrument blank, which is analyzed every 10 samples, must exhibit response < ½PQL.

Wavelength calibration checks are performed each year according to the manufacturers' instructions. The process is documented and filed with the instrument manual.

Calibration information is recorded on the computer printout of raw data and on the system hard disk. All initial calibration data are filed by run date and method number. Calibration run dates are recorded on all raw data sample records.

Conductivity Meter

The cell constant of each meter is verified, at a minimum, annually by the analysis of a KCl standard. To verify the instrument operation, a minimum of three standards and a blank are analyzed at the beginning of each working day, using KCl standards in the expected range of the sample. The standard percent recovery must be within ±10% of the known value for each standard except for the 14.9 µmhos/cm standard which must be within ±20%. For meters not having automatic temperature compensation, samples are either analyzed at 25°C ±2 °C or a manual temperature correction is employed. For meters with automatic temperature compensation, the compensation must be checked and the thermometer verified against an NIST traceable thermometer at least annually.

Total Organic Carbon (TOC)

A minimum of five calibration standards is analyzed. The concentration of the calibration standards is such that the known or expected linear response range of the instrument is bracketed. The lowest calibration point is equivalent to the practical quantitation limit.

A calibration curve is fitted to the calibration points using least squares techniques by the data processing software. In most cases, a straight-line fit can be achieved. Calibration curves must have a correlation coefficient (r) equal to or greater than 0.995. This is equivalent to a coefficient of determination (r^2) of 0.990.

The continuing calibration verification (CCV) standard is a mid-range standard that is analyzed immediately upon calibration, after every 10 samples and at the end of the analytical batch to verify that the instrument has remained in calibration during sample analysis. The acceptable range of recovery is 90-110%. If the CCV is unacceptable, the instrument must be recalibrated and verified. Sample analyses must be bracketed by acceptable calibration verification standards; therefore, all samples analyzed since the last acceptable CCV must be reanalyzed.

Calibration information is recorded on the computer printout of raw data and on the system hard disk. All initial calibration data is filed by run date and method number. Calibration run dates are recorded on all raw data sample records.

9.4.4 Gas Chromatography (GC)

Volatiles by GC

Volatile organic compounds (VOCs) are analyzed by two protocols: EPA 600 series, EPA 8000 series and references. These analyses may be performed using external standard calibration and quantitation where the absolute retention time is used to determine the identification of the target compounds.

Samples are analyzed and compounds identified using Chem Station and Mass Hunter software on GC/MS. Retention time and spectrum matching for an analyte is used for compound identification. Internal Standard compounds are set as retention time reference compounds. Bracketing by CV will be required for external standard calibrations as specified in the method or SOP. The relative retention time, as defined in the respective SOPs, is used to assist in determining the identification of the target compounds on GC/MS. Bracketing by CV will not be required unless specified in the method.

Initial calibration is performed upon instrument startup and whenever the calibration verification standard fails the acceptance criteria. A calibration curve is prepared for all target compounds with the lowest standard concentration at or below the reporting limit, which is the practical quantitation limit (PQL), and the remaining standards defining the working range of the detector. After the initial calibration standards are injected, a calibration curve is constructed using either internal standard or external standard methodology. The analyst inspects the curves before proceeding with sample analysis. Average calibration factor or average response factor is used for quantitation if the %RSD meets method criteria. Linear curves or other alternate fits spelled out in the current revision SW846 8000, may be used for quantitation; however, the correlation coefficient of a linear calibration curve must be greater than or equal to 0.99.

A mid-level calibration verification standard must be analyzed periodically as a check on the validity of the initial calibration. If the percent difference or percent drift is within the acceptance criteria, the curve is acceptable for quantitation of samples.

Volatiles QC Summary

Calibration Check	EPA 600 series	SW846 8260 series	SW846 8015C TPH - GRO
Initial calibration	Minimum of 3 standards Internal Standard	Minimum of 5 standards Internal Standard	Minimum of 5 standards External Standard
%RSD criteria [(1)]	≤35% for average response	≤20%	<20%
CCVS criteria (%Difference or %Drift)	Within response (Q)-table values found in EPA 624	≤20%	±20%
Frequency of CCVS	Each day of Operation	Every 12 hours	Every 12 hours

[(1)] Alternatively, a regression curve (linear, quadratic, etc.) may be constructed. If the correlation coefficient of the regression curve is greater than or equal to 0.99, the curve may be used for quantitation of samples.

External Standard Calibration - Samples analyzed by external standard calibration require bracketing by CCVS. If the CCVS analyzed after the samples fails to meet the acceptance criteria and the response of the midpoint standard is above the criteria (that is the response of the analytical system has increased), samples which have no target compounds detected above the PQL may be reported as Nondetects, since the compounds would have been detected if present. (SW-846 Method 8000B). Those samples with hits will be qualified with a qualifier which denotes the value is estimated.

CCVS analyzed after the samples that fails to meet the acceptance criteria due to response of the midpoint standard being below the criteria (that is the response of the analytical system has decreased), samples which have no target compounds detected above the PQL may be reported as Non-detects with a qualifier if it is demonstrated that there is adequate sensitivity to detect the analyte in the run at the PQL level. Those samples

with hits should be reanalyzed but may be reported with a qualifier which denotes the value is an estimated value.

Semivolatiles and Pesticides GC

Semivolatile organic compounds (SVOCs) and Pesticides are analyzed by two protocols: EPA 600 series, EPA 8000 series. GC/FID is utilized to screen SVOC samples for possible need of sample dilution as well as the analysis of Total Petroleum Hydrocarbons – Diesel Range Organics (TPH-DRO). GC/ECD, GC/FPD and GC/NPD are used for the analysis of Organochlorine, Organophosphorus and Nitrogen Pesticides respectively. Please refer to Pesticides 600 and 8000 analytical methods for Calibration Check QC requirements.

When internal standard calibration is used; relative retention time, as defined in the respective SOPs, as well as spectrum matching, will be used to determine the identification of the target compounds. Bracketing by CCVS will not be required unless specified in the method. If external standard calibration is used, the absolute retention time window is calculated as three times the standard deviation obtained from a 72-hour sequence or default windows of 0.03 minutes are used for compounds where the calculated window is too restrictive or zero. Bracketing by CCVS will be required for external calibrations if specified in the method or SOP.

Initial calibration is performed upon instrument startup and whenever the continuing calibration verification standard fails the acceptance criteria. A calibration curve is prepared for all target compounds with the lowest standard concentration at or below the Practical Quantitation Limit (PQL) and the remaining standards defining the working range of the detector. After the initial calibration standards are injected, a calibration curve is constructed using the internal standard or external standard methodology. The analyst inspects the curves before proceeding with sample analysis. An alternative to quantitation from an average response calibration is quantitation from a calibration curve using linear or quadratic fit or those alternate fits spelled out in SW846 8000. If the %RSD is less than or equal to the acceptance criteria, the average response factor is used for quantitation. The correlation coefficient of the calibration curve must be greater than or equal to 0.99.

A mid-level calibration verification standard must be analyzed periodically as a check on the validity of the initial calibration. If the percent difference or percent drift is within the acceptance criteria, the curve is acceptable for quantitation of samples.

External Standard Calibration - Samples analyzed by external standard calibration require bracketing by CCVS. If the CCVS analyzed after the samples fails to meet the acceptance criteria and the response of the midpoint standard is above the criteria (that is the response of the analytical system has increased), samples which have no target compounds detected above the PQL may be reported as Non detects, since the compounds would have been detected if present. (SW-846 Method 8000B). Those samples with hits will be qualified with a qualifier which denotes the value is estimated.

CCVS analyzed after the samples that fails to meet the acceptance criteria due to response of the midpoint standard being below the criteria (that is the response of the analytical system has decreased), samples which have no target compounds detected above the PQL may be reported as Non-detects with a qualifier if it is demonstrated that there is adequate sensitivity to detect the analyte in the run at the PQL level. Those samples with hits should be reanalyzed but may be reported with a qualifier which denotes the value is an estimated value.

Semivolatiles QC Summary			
SV Calibration Check	**EPA 600 series**	**SW846 8000 series**	**SW846 8015C TPH - DRO**
Initial calibration	Minimum of 3 standards Internal Standard	Minimum of 5 standards Internal Standard	Minimum of 5 standards External Standard
%RSD criteria (1)	If %RSD < 35%, linearity assumed and average RF used for SV	≤20%	≤20% for average response
CCV criteria (%Difference or %Drift)	<20% SV	±30%	±20%
Frequency of CCV	Daily	Every 12 hours	Every 12 hours

(1) Alternatively, a regression curve (linear, quadratic, etc.) may be constructed. If the correlation coefficient of the regression curve is greater than or equal to 0.99, the curve may be used for quantitation of samples.

9.4.5 Gas Chromatography/Mass Spectrometry (GC/MS)

Volatiles by GC/MS

Volatile organic compounds (VOCs) are analyzed by two protocols: EPA 600 series and EPA SW846 8000 series. These are combined into one method using in most cases the more stringent quality control of the two methods in each case. Hardware tuning is performed on each GC/MS prior to calibration as specified in the applicable EPA methods. Ion abundance acceptance criteria for VOC tuning with Bromofluorobenzene (BFB) are given below. Mass calibration is performed as an integral part of tuning. The tune check and calibration check must be performed daily for EPA 600 series and every 12 hours for SW846-8000 series. The tune analysis must meet the criteria listed in EPA methods 624 and 8260B for a 25-ng injection of Bromofluorobenzene (BFB).

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (BFB)		
Mass	**EPA 624 Ion abundance criteria**	**SW846 8260B Ion abundance criteria**
50	15-40% of mass 95	15-40% of mass 95
75	30-60% of mass 95	30-60% of mass 95
95	Base peak, 100% relative abundance	Base peak, 100% relative abundance
96	5-9% of mass 95	5-9% of mass 95
173	<2% of mass 174	<2% of mass 174
174	>50% of mass 95	>50% of mass 95
175	5-9% of mass 174	5-9% of mass 174
176	>95% but <101% of mass 174	>95% but <101% of mass 174
177	5-9% of mass 176	5-9% of mass 176

Initial calibration is performed upon instrument startup and whenever the continuing calibration verification standard fails the acceptance criteria. A calibration curve is prepared for all target compounds with the lowest standard concentration at or below the reporting limit and the remaining standards defining the working range of the detector. A minimum of 3 levels is required for the EPA 600 series and a minimum of 5 levels is required for the SW846 8000 series. A minimum of 5 levels is routinely used for volatile organics analyses.

After the initial calibration standards are injected, a calibration curve is constructed using internal standard methodology. The analyst inspects the curves before proceeding with sample analysis. The correlation coefficient of the calibration curve must be greater than or equal to 0.99 if choosing to use an alternative quantitation regression curve fit. Routinely quantitation is from an average response factor calibration curve; however the %RSD must be less than or equal to the acceptance criteria.

A mid-level calibration verification standard must be analyzed periodically (daily for EPA 600 series and every 12 hours for the SW846 8000 series) as a check on the validity of the initial calibration. If the percent difference or percent drift is within the acceptance criteria, the curve is acceptable for quantitation of samples.

Volatile GC/Initial and Continuing Calibration Check Criteria		
Method	**Initial Calibration Check Criteria**	**Continuing Calibration Check Criteria**
EPA624	All targets ≤35% RSD, or alternatively, construct calibration curve.	CCVS and QC Check Sample (20 µg/L) meets limits specified in method – EPA 624, Table 5, Range for response (Q)
SW846-8260B	Calibration Check Compounds (CCC) ≤30% RSD Target analytes <15% RSD	CCC ≤20% Difference or Drift from initial calibration
	System Performance Check Compounds (SPCCs) (minimum mean RF) Chloromethane 0.10 1,1-Dichloroethane 0.10 Bromoform 0.10 Chlorobenzene 0.30 1,1,2,2-Tetrachloroethane 0.30 (0.10 for 25-mL purge) [(1)] Others ≥0.050	

[(1)]The purging efficiency of 1,1,2,2-tetrachloroethane relative to the internal standard is such that the SPCC criteria cannot be met consistently for a 25 mL purge. The response factor is generally in the 0.1 to 0.3 range. The alternate criterion is adopted from the EPA CLP Low Level Statement of Work, a protocol similar in scope and application to SW-846 Method 8260B.

An Initial Calibration Verification Standard (ICV) is used to check the accuracy of the initial calibration curve for each compound and to insure that the standards used to generate the curve have maintained their integrity. The Calibration Verification Standard (CCVS) is analyzed every time the instrument is calibrated and every 12 hours shift. The CCVS also contains the Calibration Check Compounds (CCCs) and System Performance Check Compounds (SPCCs) so that these checks can be accomplished in a single analysis.

Method 8260B - After the CCCs and SPCCs are evaluated, all target compounds are evaluated for linearity. If the %RSD is less than or equal to 20%, the average response factor can be used for quantitation. If the %RSD exceeds 20%, a regression curve (linear, quadratic, etc.) may be used for quantitation if the correlation coefficient is greater than 0.99.

Each instrument is calibrated according to the procedures specified within the relevant EPA method. In all cases, the minimum requirements and specifications given in the methods are met or exceeded. A brief description of the calibration requirements and practices of the laboratory are discussed here. Refer to the specific EPA method protocols for additional details.

The internal standard responses and retention times of each standard and sample analyzed are evaluated after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from

retention times in the most recent CV, then the chromatographic system must be inspected for malfunctions and corrections must be made. If the response for any internal standard varies by more than a factor of two (-50% to +100%) from the most recent calibration sequence, the GC/MS system must be inspected for malfunctions and corrections must be made, as appropriate. Any standard or sample failing these internal standard checks are re-analyzed. The system is re-calibrated, if necessary.

Analytical standards for the internal standards, surrogates, initial calibration, continuing calibration check, system performance check standards and standard spiking solutions must be certified and NIST- traceable. The standard solutions for the calibration and matrix spiking solutions must be from independent sources. The term "independent source" means that the origin of the standard preparations are known to be different from one another. In practical terms this requires that the solutions be prepared by two different suppliers or at a minimum, have different lot numbers from the same supplier.

Paper copies of the calibration and quantitation reports are stored in a file folder labeled appropriately. All raw electronic data files are initially stored on the MS system hard disk, then later archived to CD or flash drive for permanent storage.

Semivolatiles by GC-MS

Semivolatile compounds are analyzed by two protocols: EPA 600 series and EPA SW846 8000 series. Hardware tuning is performed on each GC/MS prior to calibration as specified in the applicable EPA methods. Ion abundance acceptance criteria for SVOC tuning with a 50-ng injection of Decafluorotriphenylphosphine (DFTPP) are given below. Mass calibration is performed as an integral part of tuning. The tune check and calibration check must be performed daily for the 600 series and every 12 hours for the 8000 series. The tune analysis must meet the criteria listed in EPA methods 625 and 8270D for a 50-ng injection of Decaflourotriphenylphosphine (DFTPP).

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (DFTPP)

Mass	EPA 625 Ion Abundance Criteria	SW846 8270D Ion Abundance Criteria
51	30-60% of mass 198	10-80% of mass 198
68	<2%of mass 69	<2% of mass 69
69	(reference only)	(reference only)
70	<2% of mass 69	<2% of mass 69
127	40-60% of mass 198	10-80% of Base Peak
197	<1% of mass 198	<2% of mass 198
198	Base peak, 100% relative abundance	Base peak, or > 50% of mass 442
199	5-9% of mass 198	5-9% of mass 198
275	10-30% of mass 198	10-60% of Base Peak
365	>1% of mass 198	>1% of mass 198
441	Present but less than mass 443	Present but < 24% mass 442
442	>40% of mass 198	Base peak or 540% of mass 198
443	17-23% of mass 442	15-24% of mass 442

Initial calibration is performed upon instrument startup and whenever the continuing calibration verification standard fails the acceptance criteria. A calibration curve is prepared for all target compounds with the lowest standard concentration at or below the reporting limit and the remaining standards defining the working range of the detector.

After the initial calibration standards are injected, a calibration curve is constructed using internal standard methodology. The analyst inspects the curves before proceeding with sample analysis. Quantitation is from

an average response factor; however, the %RSD must be less than or equal to the method acceptance criteria to use average response factor . An alternate calibration curve, a regression curve (linear, quadratic, etc.) may be used for quantitation if the correlation coefficient is greater than or equal to 0.99.

A midpoint calibration verification standard must be analyzed periodically as a check on the validity of the initial calibration. If the percent difference or percent drift is within the acceptance criteria, the curve is acceptable for quantitation of samples.

Semivolatiles GC/MS Initial and Calibration Verification Check Criteria		
Method	**Initial Calibration Check Criteria**	**Calibration Verification Check Criteria**
EPA 625	All targets ≤35% RSD, or alternatively, construct calibration curve.	All targets ≤20% difference from initial calibration.
SW846 8270D	≤20% RSD for average response calculations; Analytes meet minimum response given in Table 4 SW 846 8270D for each level; if no response given use default of 0.01.	RFs should not differ more than 20% from average response of initial calibration; concentration should be within 30% of expected concentration. Analytes meet minimum responses given in Table 4 SW 846 8270D if no response given use default of 0.01.

SW-846 Method 8270D - The average response factor is used for quantitation if the %RSD is less than or equal to 20%. Alternatively, a regression curve (linear, quadratic, etc.) may be used for quantitation if the correlation coefficient is greater than 0.99.

Each instrument is calibrated according to the procedures specified within the relevant EPA method. Clarification of the calibration requirements and practices of this laboratory are discussed here. Refer to the specific EPA method protocols for additional detail.

The internal standard responses and retention times of each standard and sample analyzed are evaluated after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last curve, the chromatographic system must be inspected for malfunctions and corrections must be made. If the response for any internal standard varies by more than a factor of two (-50% to +100%) from the last mid-point of the curve or daily CCVS which should be within 50% to 200 % of the of the internal standard responses of the mid-point standard of the curve, the GC/MS system must be inspected for malfunctions and corrections must be made, as appropriate. Any standard or sample failing these internal standard checks is re-analyzed. The system is re-calibrated, if necessary. Sample is qualified with appropriate qualifier if reported.

Analytical standards for the internal standards, surrogates, initial calibration, continuing calibration, QC check standards and standard spiking solutions must be certified and NIST- traceable. The standard solutions for the calibration and QC Check Standard must be from independent sources. In practical terms this requires that the solutions be prepared by two different suppliers or at a minimum, have different lot numbers from the same supplier.

Paper copies of the calibration and quantitation reports are stored in a file folder labeled with the initial calibration data file name. All raw electronic data files are initially stored on the MS system hard disk, and then later archived to a CD or flash drive for permanent storage.

9.5 Standardization of titrating solutions

The titrants for all titrimetric procedures are standardized against primary standards before each use. Table 9-3 shows standardization of titrating solutions.

Table 9.1. Calibration Frequency, Procedures, Standards, and Acceptance Criteria for Support Equipment

Instrument/Analyte	Frequency	Procedure	Standard	Acceptance Criteria
pH Meter (primarily for Color and Alkalinity analyses)	Daily	Calibration (2 points)	Vendor Certified Buffer Solutions	Within Certified Values
	Daily	Third buffer Check	Vendor Certified Buffer Solution	± 0.1 pH units
Analytical Balances	Daily	Calibrated according to manufacturer's instructions		Manufacturer specified
	Daily	1 point verification	ASTM 1 and 2 or equivalent weights	ASTM tolerances
	Quarterly	3 point verification	ASTM 1 and 2 or equivalent weights	ASTM tolerances
Ovens	Daily	Temperature checked and recorded	NIST traceable	Varies according to use - see determinative SOP
Incubators	Twice Daily	Temperature checked and recorded	NIST traceable	Varies according to use - see determinative SOP
Autoclaves	Daily	Maximum temperature and pressure recorded	NIST traceable and pressure gauge	Varies according to use - see determinative SOP
Water baths	Daily	Temperature checked and recorded	NIST traceable	Varies according to use - see determinative SOP
Refrigerators	Daily	Temperature checked and recorded	NIST traceable	1 to 6°C with no evidence of freezing
Freezers	Daily	Temperature checked and recorded	NIST traceable	-10°C to - 20°C
Thermometers, Hg or spirit-filled	Annually	Verified against an NIST or NIST traceable thermometer	NIST traceable	Varies according to use - see thermometer calibration SOP or log
Thermometers, Digital	Quarterly	Verified against an NIST or NIST traceable thermometer	NIST traceable	Varies according to use - see thermometer calibration SOP or log
Thermometers, NonContact	Annually	Verified against an NIST or NIST traceable thermometer	NIST traceable	± 2 °C
Pipettors	Quarterly	Verified gravimetrically	Class ASTM 1 &2 or equivalent weights	±1%, 2% and 5% of full scale volume

Table 9.2. Calibration Frequency, Procedures, Standards, and Acceptance Criteria for Operational Equipment

Instrument/Analytes	Frequency	Procedure	Standard	Acceptance Criteria
AA spectrophotometer -metals (flame) -metals (furnace) -mercury (cold vapor)	Daily or failure of CCVS	Calibration (4-6 points)	Vendor certified standard. Plasma grade-ICP	Correlation coefficient >0.995
	Immediately following calibration, 10% and end of run	ICV/CCVS	Mid-range calibrant	±5% of initial value, then ±10% after every 10 samples and at tend of run
ICP spectrophotometer	Daily following calibration	Second source QCS	Certified reference material	±10% of true value
Leeman Mercury analyzer AFS	Daily following calibration	Second source QCS	Certified reference material	
Ion chromatograph	Daily or failure of ICV/CCVS	Calibration (3-5 points)	Vendor certified standards	Correlation coefficient > 0.995
	Immediately following calibration and end of run.	CCVS	Mid-range calibrant	±5% initially ±10% thereafter
Autoanalyzers	Daily	Calibration (6-8 points)	Reagent grade chemicals	Correlation coefficient > 0.995
	10% and end of run	CCVS	Mid-range calibrant	±10%
	10-20%	Second source QC	Certified reference material	Within certified values
	10% and end of run	Cd column check	Nitrate standard	±10% of true value
pH meter	Daily	Calibration (2-3 points)	Vendor certified buffers	Within certified values
	Following calibration	Mid-point check	Vendor certified buffers	Within ±0.1 pH units
Conductivity meter	Daily	Calibration verification (3 points)	Vendor certified standards	±10% of certified values
	Annually	Cell constant verification	Vendor certified standards	±10% of certified values
Spectrophotometer	Daily/Annually	Calibration (3 points for daily or 5 points for annual)	Vendor certified standards	Correlation coefficient >0.995
	Daily	Second source QC	Certified reference material	±10% of certified value
Turbidity meter	Daily	Calibration check (Each range used)	Secondary sealed standard	±10%
	Monthly	Calibration (3 NTU levels)	Primary calibration standards	±10%
DO meter	Weekly	Barometric pressure calibration	Barometer	
Fluorometer	Daily	Calibration (1 point)	Chlorophyll *a* standard	±10%
	Daily	QCS	Chlorophyll *a* standard	±5%
GC Semivolatiles	Initially and every 12	Injection port contamination check	Solvent check	no contamination present
	Initially or upon failure of QC criteria acceptance	Calibration (3 to 5 points)	Vendor certified standards	Coefficient of determination >0.990
	After initial calibration	Second source standard	Vendor certified standard	≤20% difference

Table 9.2. Calibration Frequency, Procedures, Standards, and Acceptance Criteria for Operational Equipment

Instrument/Analytes	Frequency	Procedure	Standard	Acceptance Criteria
	Every 12 or hours	CCVS	Mid-level standard	≤20% difference
GC Volatiles	Initially or upon failure of CCC	Calibration (5 points)	Vendor certified standards	Coefficient of determination >0.990
	Every 12 or 24 hours	CCC	Mid-level standard	<15% difference
	Every run or every 12 hours	Second source standard	Vendor certified standard	<20% of true value
GC/MS Semivolatiles	Every 12 hours during a run	Instrument tune	DFTPP	Method specified criteria
	Initially, upon exceedance of criteria for acceptable daily verification and every 12	Calibration (3 to 6 points)	Vendor certified standards	minimum RF as spelled out in Table 4 of 8270D (if analyte not listed use default minimum response of **0.01**
	After initial calibration	Second source QC	Vendor certified standard	≤20% difference
GC/MS Volatiles	Every 12 hours during a run	Instrument tune	BFB	Method specified criteria
	Initially and upon failure of CCC	Calibration (3 to 5 points)	Vendor certified standard	%RSD for each CCC must be ≤ 30%
	After initial calibration and end of every 12	Second source QC	Vendor certified standard	≤20% difference from initial calibration
	Every 12	CCC	50 ppb calibrant	<20% difference form initial calibration
	Every 12	SPCC	50 ppb calibrant	Minimum RF 0.30 for two and 0.10 for three
Fluoride meter	Daily	Calibration (3 points)	Vendor certified standard	Correlation coefficient > 0.995
	Daily	Second source QC	Vendor certified standard	Within certified value
	Daily	Slope check	Calibrants	54 ± 4 mV
TOC analyzer	Daily	Calibration (3 points)	Vendor certified standard	Correlation coefficient > 0.995
	Daily	Second source QC	Vendor certified standard	Within certified value
ICP/MS	Daily or failure of CCVS	Calibration-each batch (5points)	Vendor certified standard.	Correlation coefficient >0.995
	Immediately following calibration, 10% and end of run	ICV/CCVS	Mid-range calibrant	±10% of initial value after calibration then ±15% after every 10 samples and at end of run.
	Daily following calibration and at end of run.	Second source QCS	Certified reference material	±15% of true value

Table 9.3. Standardization of Titrating Solutions.

Titrating Solution	Primary Standard	Source of Primary Standard	Frequency of Standardization	Methods/Reference
Sulfuric Acid	Sodium carbonate solution	Commercial supplier	Every 7 days.	Alkalinity by Titration, SM 2320B-1997 Editorial revisions 2011
EDTA	Calcium carbonate solution	Commercial supplier	Each day of use.	Hardness by EDTA Titrimetric, SM 2340C-1997
Formaldehyde	0.1N HCl	Prepared and standardized lab from reagent grade source	Every six months	ASTM D6303-98

10.0 Preventive Maintenance

The Central Laboratory is equipped with mechanical and computerized instrumentation. A preventive maintenance schedule has been developed to minimize instrument downtime and to obtain reliable data over the life of the instrument. Analysts and supervisors are primarily responsible for routine maintenance and repair of the instruments. Service agreements are kept for some major instruments in the laboratory. Major repairs that go beyond the expertise of the analysts, Supervisors and Managers are contracted to external specialists.

Table 10.1 lists the types of analytical equipment utilized to perform analyses and the frequency of routine preventive maintenance tasks performed to ensure data quality. The service intervals are designated as follows: D = daily; W = weekly; M = monthly; Q = quarterly; SA = semi-annually; A = annually; AN = as needed. The preventive maintenance schedules are based primarily on manufacturer guidance, recommendation in the literature, and the experience of the analysts, Supervisors and Managers. Some of the items will be performed as an integral part of each procedure. Others will be followed as closely as possible, balancing to the extent possible the workload and the urgency of the need for preventive maintenance. Common sense and familiarity with the performance of each instrument will dictate whether the preventive maintenance schedule needs to be accelerated or delayed for that instrument. Trends and excursions from accepted quality assurance requirements such as QC sample results, degradation of peak resolution, a shift in the calibration curve, and loss of sensitivity are monitored to determine if there is instrument malfunction, and in such cases preventive maintenance is provided on an as-needed basis.

10.1 Documentation

An instrument maintenance logbook documenting instrument problems, instrument repair and maintenance activities are kept for all major pieces of equipment. It is the responsibility of each Unit Supervisor to ensure that instrument maintenance logs are up to date for all equipment in his/her Unit. Documentation must include all major maintenance activities such as contracted preventive maintenance and service, and in-house activities such as the replacement of electrical components. An extensive spare parts inventory is maintained for routine repairs at the laboratory facilities, consisting of GC columns, AA lamps, fuses, printer heads, tubing, and other instrument components.

Logbook entries must include the date, the problem, the corrective actions taken, the name of the person performing the service and, when appropriate, a statement that the instrument has returned to control and is available for use (also state what was used to determine a return to control - e.g., CCVS acceptable). When maintenance or repair is performed by an outside agency, service receipts detailing the service performed can be stapled into the logbooks adjacent to pages describing the maintenance performed.

10.2 Contingency Plan

The laboratory has several pieces of analytical equipment in duplicate. This redundancy allows the laboratory to keep performing critical analyses on one instrument while the other is out of service.

In the event of instrument failure or if critical holding times are approaching, the following options exist:

1. Portions of the sample load may be diverted to duplicate instruments within a facility.
2. The analytical technique may be switched to an alternate approved technique (e.g., Total Hardness by ICP to titration).
3. Samples may be shipped to another State lab. When shipping samples to another facility, COC procedures are followed as required.

In the event of equipment malfunction that cannot be resolved, service shall be obtained from the instrument vendor manufacturer, or qualified service technician, if such a service can be tendered. If on-site service is unavailable, arrangements shall be made to have the instrument shipped back to the manufacture for repair. Back up instruments, which have been approved for the analysis, shall perform the analysis normally carried out by the malfunctioning instrument. If the backup is not available and the analysis cannot be carried out within the needed timeframe, sample collection personnel may be asked to postpone sampling events or to send the samples to a certified commercial laboratory.

Any item of equipment which has been subjected to overloading or mishandling, which gives suspect results, or has been shown to be defective shall be taken out of service. The instrument will be clearly identified and, wherever possible, stored

in a different location until it has been repaired and shown by calibration, verification or test to perform satisfactorily. The supervisor shall examine the effect of this defect on previous calibrations or tests.

10.3 Uninterruptible Power Supply

As a further precaution, the Central Laboratory keeps some major instrumentation connected to individual Uninterruptible Power Supply (UPS) units which provide line conditioning and backup power.

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
1.) WET CHEMISTRY								
UV/VIS Spectrophotometers (Shimadzu, 1601, 1700)								
Wavelength	X				X			Verify wavelength(s)
Cells	X							Inspect daily for chips/scratches
Lamps							X	Replace if blown and realign
Flow Injection Auto Analyzers								
FIA8000								
Cells		X						Inspect for chips/scratches
Lamps		X						
Consumables parts		X						
Fluorometer (Turner Designs)								
Meter	X							Calibrated with primary standard and checked with secondary standard (solid)
Lamp							X	Replace if blown and realign
Analytical Balances (Sartorious)								
Balance Calibration	X							Verify calibration with ASTM 1 & 2 weights
Balance						X		Checked and adjusted by service contractor
Weights						X		Checked against ASTM 1 &2 weights
Centrifuges (Beckman Coulter)								
Centrifuge operation							X	Check warranty
Compartment							X	Clean
8” Drill Press benchtop (Chlorophyll grinder)								
Drill press operation		X						
Thermometers								
Hach COD Reactor					X	X		Verify against NIST traceable
Convection Ovens					X	X		Verify against NIST traceable
Waterbaths								
Compartment							X	Clean with hot soapy water, fill with DI water
Thermometer					X	X		Verify against NIST traceable

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Freezer								
Cleaning						X	X	Defrost and clean with hot soapy water
Thermometer					X	X		Verify against NIST traceable
Cooler								
Cleaning		X	X					
Stored samples		X						Discard samples by Discard List
Thermometer					X	X		Verify against NIST traceable
Flow Injection Auto Analyzers and Ion Chromatograph (Lachat)								
Flow cell – flare tubing and o-rings				X				Replace.
Manifold Tubing				X				Replace.
Pump Tubing	X	X	X					Replace.
Manifold / Valve o-rings				X	X			Replace.
Pump and pump cartridges			X					Inspect and Clean.
Transmission / Waste tubing					X		X	Replace.
pH Meter								
pH buffer standards	X							Check holding time and replace
PROBE	X							When not in use, keep lower end of probe in beaker of standard 4.0.
ATC							X	Verify with NIST traceable
Filling solution	X							Inspect daily
Filling solution		X						Top off Weekly
LCD Screen		X				X		Clean
Calibrated	X							Or when used
Dionex ICS5000 1 and 2								
Consumable		X	X			X		Monitor daily, clean , replace if needed
EG, DP pumps, autosampler, values, needles		X	X			X		Monitor daily, clean , replace if needed
AS-AP Auto Sampler		X	X			X		Monitor daily , clean , replace if needed
ICS 5000							X	Preventive Maintenance every 18 month
Heidolph, Laboratory 4010								
Clean	X							Post usage
Minerals deposit clean up							X	

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
n-Hexane	X							Dispose post usage
2.) NUTRIENTS								
Flow Injection Auto Analyzers and Ion Chromatograph (Lachat)								
Flow cell – flare tubing and o-rings						X		Replace.
Manifold Tubing						X		Replace.
Pump Tubing				X				Replace.
Manifold / Valve o-rings					X			Replace.
Pump and pump cartridges			X					Inspect and Clean.
Transmission / Waste tubing							X	Replace.
Cadmium column							X	Replace.
Autoclave								
Pressure verification	X							Check and document; replace seals as needed.
Temperature verification	X							Check with autoclave thermometer; document
Cleaning					X			Wash with soapy water if needed; inspect for leaks and degradation.
Seals							X	Visually inspect and replace as needed.
Timing						X		Check with stopwatch
Block Digestor								
Digestion Block		X						Inspect and clean using DI water.
Digestion Tubes							X	Replace with new tube(s).
Digestion Tubes	X							Clean and check for cracks.
Exhaust manifold	X							Rinse with DI water (after use)
Tube Rack			X					Clean with DI water & tissue paper.
Distillation System								
Hot Block							X	Clean with DI water & tissue paper
Tube caps, manifold tubes							X	Rinse with DI water after use
Distillation tubes, glassware							X	Wash after each use; air dry
pH Meter								
Probe			X					Inspect; clean or replace if needed
Probe	X							When not in use, keep lower end of probe in beaker of standard 4.00.

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
pH buffer standards							X	Prepare/purchase as needed.
ATC						X		Verify with NIST thermometer
Nutrients Continued								
Digital & Top-Loading Balances								
Balance Pan							X	Clean (DI water & tissue paper).
Balance Level	X							Verify that balance is level.
Calibration	X							Check with standard weights each day used
Balance						**X**		Contract service/cleaning
Weights						**X**		Verify against ASTM weights 1 and 2
Ultrasonic Cleaner								
Water in Tank	X							Maintain correct level; renew water as needed
Tanks							X	Empty, clean with warm water, and wipe with non-abrasive cloth.
Reagent/Standard Refrigerator								
Temperature	X							Verify temperature with thermometer
Shelves					X			Clean
3.) MICROBIOLOGY								
BOD Meter								
Probe (electrolyte)		X						Change solution.
Probe (membrane)							X	Replace membrane.
Barometer			X					Calibrate.
Turbidimeter								
Meter	X							Verify calibration with sealed standards.
Lamp							X	Replace.
Meter			X					Calibrate with sealed HF Scientific standards
TOC Analyzer								
Carrier gas.	X							Check flow. Should be 200 cc/min $\pm$10%
DDI H_2O	X							Replace.
Corrosive scrubber (Cu+ Sn)	X							Check for tarnish. Replace as needed

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
8-port valve thumbscrews	X							Hand-tighten.
IC sparger		X						Clean with mild soap and water.
Microbiology continued								
Sparger & water traps	X							Empty.
Permeation dryer	X							Inspect for damage or water accumulation.
Combustion tube or catalyst							X	Change or repack.
Baseline							X	Adjust.
Microscope								
Lens							X	Clean.
Lamp							X	Replace.
Incubator (Coliform)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Coils						X		Clean coils
Analytical Balance								
Balance Calibration	X							Verify calibration with ASTM weights 1 and 2 weights
Balance						X		Contract service/cleaning
Weights						X		Verify against ASTM weights 1 and 2 weights
Autoclave								
Pressure verification	X							Check and document; replace seals as needed.
Temperature	X							Check and document
Temperature verification		X						Check with maximum hold thermometer
Cleaning			X					Wash with soapy water; visually inspect for leaks and degradation.
Seals							X	Visually inspect and replace as needed.
Timing				X				Check with stopwatch; replace as needed.
4.) METALS								
ICP – Optima 3000 XL								
Pump tubing	X							Replace every 8 hours of operation.

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Peristaltic pump and drain	X							Check that drain tube is firmly attached to spray chamber drain fitting and liquid flows smoothly through pump.
Metals Continued								
Inspect waste and rinse water fluid levels	X							Empty or fill as needed.
Nebulizer							X	Clean.
Filters			X					Inspect monthly, clean or replace as needed.
Spray Chamber							X	Clean.
Optical Window			X					Clean or replace if needed.
Quartz torch							X	Clean and align.
Circulating cooler		X						Check water supply and for dust buildup on cooling coils.
Replace torch							X	Replace with new quartz tube and o-rings. Perform X-Y align.
Air Supply for Shear Gas	X							Check pressure and for condensation in traps. Output pressure should be a minimum of 60 PSI.
Liquid argon tanks attached to manifold system	X							Insure gas supply will last the day and there is sufficient pressure (90-120 PSI).
Nitrogen Tank	X							Insure gas supply will last the day. Output pressure should be a minimum of 40 PSI.
THGA Graphite Furnace and AS-800 Autosampler								
Graphite tubes	X							Inspect for deposits around injection hole and cracks in tube. Clean or replace as needed.
Graphite contacts	X							Inspect for deposits and cracks in the contacts. Clean or replace as needed.
Furnace windows							X	Clean or replace as needed.
Water level in cooling system		X						Make sure water level is at the max.
Autosampler external surfaces		X						Wipe over the surfaces with a damp lint-free cloth
Complete rinsing system	X							Fill and flush the rinsing system before the start of every analysis run.

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Valves							X	Clean or replace seals, valves are covered under maintenance agreement.
Wash bottle	X							Check daily and empty as needed.
Rinse bottle	X							Make sure rinse bottle is filled with 18-MΩ water.
Metals continued								
Pipet tip	X							Check pipet tip for damage and repair or replace.
Argon gas	X							Outlet gauge minimum pressure is 50 PSI and maximum 58 PSI.
(UHP or 99.996% purity)								
Special gas (95% Ar + 5% H)	X							Outlet gauge minimum pressure is 50 PSI and maximum 58 PSI.
Mercury Analyzer FIMS 400								
Pump tubing	X							Inspect daily and replace as needed.
FIMS-cell window							X	Measure the absorbance of the cell windows regularly, if >0.75, clean.
FIMS-cell inner surface							X	Clean if sensitivity drops not attributable to other factors.
Air filter						X		Replace sooner if needed.
Waste bottle	X							Empty after each analytical run.
FIAS-valve							X	Take apart and clean per maintenance manual.
Argon gas(UHP or 99.996% purity)	X							Outlet gauge pressure is 52 PSI.
Fume trap (for fumes emitted from FIMS-cell)	X							Change charcoal in trap as needed.
Elan 6100 ICP/MS								
Pump tubing	X							Replace every 8 hours of operation.
Peristaltic pump and drain	X							Check that drain tube is firmly attached to spray chamber drain fitting and liquid flows smoothly through pump.
Nebulizer							X	Clean.
Filters			X					Inspect monthly, clean or replace as needed.
Spray Chamber							X	Clean.
Liquid argon tank	X							Insure gas supply will last the day and there is sufficient pressure (90-120 PSI).

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Inspect waste and rinse water fluid levels	X							Empty or fill as needed.
Inspect roughing pump oil level and cooler	X							Add or change if dark brown color.
Inspect condition of drain and rinse station pump tubing							X	Replace if needed.
Metals continued								
Vacuum pressure (Plasma On)	X							Pressure should be around 1.60E-05. Lower pressure may require interface cones to be replaced.
Daily performance check	X							Take corrective actions necessary to pass. See table below.
Daily performance check list								Analyte / Mass (amu) / Intensities (cps) Mg / 4 / >20,000 Rh / 102.9 / >150,000 In / 114.9 / >300,000 Pb / 208 / >100,000 Ba++/Ba+ / 69 / <0.03 CeO/Ce / 155.9 / <0.03 Bkgd / 220 / <30
X-Y optimization							X	Usually after changing torch = or interface cones.
Nebulizer optimization							X	To increase sensitivity.
Auto lens optimization							X	To increase sensitivity and after changing out the lens.
Mass calibration and resolution			X					Use tuning solution and instrument software to calibrate the mass and adjust peak resolution.
Dual detector calibration							X	Use multi-element standard solution and software to perform dual detector calibration
Circulating cooler		X						Check coolant and for dust buildup on cooling coils.
Leeman mercury analyzer AFS								
Waste Jug	X							Empty after every run
Reductant bottle	X							Clean threads as necessary
Acid Rinse bottles	X							Inspect for cracks
Pump Tubing	X							Change after every run or every pair of runs.

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Process tubing, waste drain tubing waste line, sample tip and tubing assembly, reactor mix tubing, reductant bottle tubing, rinse bottle tubing.	X							Inspect for leaks. Change if tubing becomes cloudy.
(Metals Continued) Pump head	X							Disassemble and apply oil if pump hesitates or binds up when starting pump while pump tubing is clamped down and at running tension. Check that liquids flow smoothly through pump.
Pump Cassettes	X							Inspect for wear and broken parts. Replace if needed. Clean off grease deposits.
Air filter		X						Wash, dry and replace as needed.
Argon supply	X							Insure that pressure gauge is at 80 psi.
Liquid gas separator		X						Replace when liquid containment area becomes cloudy.
Mercury lamp	X							Replace when indicated due to poor instrument performance.
Optical cell							X	Disassemble and clean as needed due to impaired instrument performance.
Nafion dryer							X	Replace as needed due to impaired instrument performance.
Soda lime tube	X							Clean and dry in oven as needed.
Gold traps	X							Replace as needed as indicated by uneven heating, poor peaks or poor instrument performance.
Soda lime dryer assembly	X							Replace tubing if kinking occurs at the base of the unit. Replace assembly if O-rings fail to seal.
Autosampler	X							Clean and oil rods as needed for smooth, silent movement.
Performance check	X							Compare calibration intensities with recent calibration intensities. Observe peaks for anomalies.
5.) VOLATILE ORGANICS								
Gas Chromatograph/FID								
FID							X	Clean, replace jet
Syringe						X	X	Replace as needed
Chromatographic column							X	Replace or cut as needed.
Leak check							X	Check column and fittings as needed/drift or poor sensitivity

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Inlet Septum							X	Replace as needed.
Gas Cylinders	X						X	Inspect daily, change when pressure reads < 500 psi.
Hydrocarbon/Moisture Trap							X	Replace.
Teflon transfer line							X	Replace as needed.
Heated transfer lines							X	Bake as needed.
Gas Chromatograph/Mass Spectrometer - VOA								
Inlet septum							X	Replace as needed
GC Column							X	Replace/cut as needed/poor sensitivity
Filament							X	Replace as needed/poor sensitivity
MS Source							X	Clean as needed/poor sensitivity
Leak check pumps			X					Inspect visually and Standard Spectral Tune
Pump fluid					X			Replace pump fluid
Calibration vial					X			Check level and refill as needed.
Inlet liner and O-rings							X	Replace as needed/contamination
System check		X						Standard Spectral Tune
Check gas flow							X	As needed
Gas Cylinder	X							Inspect daily, change when pressure reads <500 psi.
Hydrocarbon/Moisture Trap							X	Replace.
Disposable purge tubes	X							Replace
Sorbent trap							X	Change as needed/poor sensitivity
Purge flow					X			Inspect semi-annually; adjust as needed.
Rinse purge ports	X							Use charcoal filtered water.
Leak check lines							X	As needed/poor sensitivity
Bake system and transfer lines							X	As needed/ contamination
6.) PESTICIDES								
Gas Chromatograph - PESTICIDES								
Column							X	Replace.
Syringe	X						X	Inspect, replace
Septum		X						Replace
Wash Bottles	X						X	Inspect, refill, replace, clean

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
ECD							X	Replace or have serviced as needed due to impaired instrument performance
FPD							X	Replace photomultiplier tubes as needed due to impaired instrument performance.
NPD							X	Replace beads as needed due to impaired instrument performance.
Gas Cylinder	X							Inspect daily, change when pressure reads < 300 psi.
Check gas leaks							X	After column change or signs of leak
Hydrocarbon/Moisture Trap							X	Replace.
Inlet liner			X					Replace
Automated Sample Processing System (GPC)								
Column							X	Re-solvate.
Gas Cylinder	X							Inspect daily, change when pressure reads <300psi.
Methylene Chloride reservoir	X							Add solvent.
6.)SEMIVOLATILE ORGANICS								
Gas Chromatographs - SVOA								
Column			X				X	Cut off 1 foot or Replace.
Septum			X				X	Replace
Gas Cylinder	X						X	Inspect gauge change when pressure reads < 200 psi.
Hydrocarbon/Moisture Trap							X	Replace.
Inlet, inlet liner			X				X	Clean, replace and clean
FID						X	X	Clean, replace jet
Wash Bottles	X						X	Inspect, refill, replace, clean
Syringe	X						X	Inspect, replace
Check gas leaks							X	After column change
Mass Spectrometer - SVOA								
Check DFTPP.u tune setting with cal gas snap shot	X							Check base line operation, air leaks, tighten vacuum system
Vacuum Pump		X				X	X	Check oil level, change oil
Ion source	X						X	Check, Clean when performance not in controls

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
7.) ASHEVILLE REGIONAL LABORATORY								
BOD Meter								
Probe (electrolyte)		X						Change solution
Probe (membrane)							X	Replace membrane
Barometer			X					Calibrate
Asheville Regional Laboratory continued								
Turbidimeter								
Meter	X							Verify calibration with sealed standards
Lamp							X	Replace
Meter			X					Calibrate with sealed HF Scientific standards.
Microscope								
Lens							X	Clean.
Lamp							X	Replace.
Orion 920A Meter								
pH Probe							X	Clean, add filling solution
Ammonia Probe		X						Change membrane & filling solution
ATC						X		Calibrate against NIST traceable thermometer
Analytical Balance								
Balance Calibration	X							Verify calibration with ASTM weights 1 and 2 weights
Balance						X		Contract service/cleaning
Weights						X		Verify against ASTM weights 1 and 2 weights
Balance Pan	X							Clean
Balance Level	X							Check that balance is level
DI Water System								
Filters							X	Change.
System							X	Contract service.
Autoclave								
Pressure verification	X							Check and document; replace seals as needed
Temperature	X							Check and document

Table 10.1. Laboratory Equipment Preventive Maintenance Schedule

	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Temperature verification		X						Check with maximum hold thermometer
Cleaning			X					Wash with soapy water; visually inspect for leaks and degradation; add DI water
Seals							X	Visually inspect and replace as needed
Timing				X				Check with stopwatch
Asheville Regional Laboratory continued								
Incubators (BOD)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST traceable thermometer
Compartment			X					Clean
Coils						X		Clean coils
Incubator (Coliform)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST traceable thermometer
Compartment			X					Clean
Coils						X		Clean coils
Refrigerators (sample storage)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST traceable thermometer
Compartment			X					Clean
Coils						X		Clean

D – Daily, W- Weekly, M- Monthly, Q – Quarterly, A- Annually, SA – Semi-Annual, AN – As Needed

11.0 Quality Control Checks to Assess Precision and Accuracy and Calculation of Method Detection Limits

The key to a successful QA/QC program is strict adherence to the program during all phases of the project including pre-sampling discussions, sample collection, preservation, storage and analysis, and validation and reporting of results. Field and laboratory quality control checks are a part of each sampling trip and laboratory analysis. Quality control checks are used to establish quality assurance objectives in the laboratory (see Section 5). Once the quality assurance objectives are set, QC samples and elements are used to continuously monitor the quality of the data against those objectives. By using laboratory QA targets and QC check results, the user knows the limits of data precision and accuracy and if these objectives were met for a given set of data.

11.1 Quality Control (QC) Checks

Quality Control samples must be scheduled with each batch of samples of a given matrix analyzed for a given parameter. This section discusses the QC checks used by the Water Sciences Section Chemistry Laboratory on a routine basis. However, the analytical methods used and, occasionally, the client define the QC checks that are required for each test. If the quality control requirements of a particular method or client are more stringent than those presented here, the requirements of that method or client will be followed.

11.1.1 Field QC Checks

When field QC sample collection and analysis are required for a project, it is the responsibility of the sampling personnel to ensure that this sampling is performed correctly and at the required frequency. Field QC samples may or may not be identified as such to the laboratory and are considered by the laboratory as field samples for the purpose of QC batching, sample preparation and analysis. Field QC sample results are reported in the same manner as actual field samples, unless a specific deliverable is requested by a client. No correction of the analytical data for associated field samples is done in the laboratory based on the analysis of field QC samples. Recommended field QC may include field duplicates, split samples, field blanks, filter blanks, equipment blanks and trip blanks.

The following field QC blanks are required for sample submission to the Water Sciences Section Laboratory:

- A Field Blank must accompany every sample for Low-Level Mercury
- A Filter Blank must accompany every set of samples for DOC
- A Trip Blank must accompany every set of samples for VOA

When samples or sample sets for these parameters are received without an associated field QC blank, a Sample Condition Upon Receipt report is completed and the collector is notified immediately of the infraction. Re-sampling is generally recommended. Any contamination problem discovered in a trip blank initiates an immediate investigation which generally involves comparison with the associated batch method blanks and discussion with the sample submitter.

A description of the preparation and handling of trip blanks follows:

Trip Blanks

Volatile organic samples are susceptible to contamination by diffusion of organic contaminants through the septum of the sample vial. A trip blank must accompany the collector of the volatile organic samples from origin of trip to submission to volatiles unit. The purpose is to determine if contamination has occurred as a result of improper sample container cleaning, contaminated blank source water, sample contamination during storage and transportation due to exposure to volatile organics (e.g., gasoline fumes) and other environmental conditions during the sampling event and subsequent transportation to the lab.

Trip blanks are prepared prior to the sampling event either by the laboratory providing sample containers, or by sample collection personnel who are responsible for the initial preparation of sample containers and

field equipment. Trip blanks are prepared by filling three (3) 40-mL VOA vials (with no headspace) with organic-free water. Any appropriate preservatives must be added at the time that the blanks are prepared. The sample containers are sealed, labeled appropriately, and transported to the field in the same manner as the sample vials. These blanks are NOT to be opened in the field. They are to be transferred to the sample cooler and transported with the samples to the laboratory. Trip blanks are prepared for each cooler expected to be used to store and transport VOA samples.

11.1.2 Laboratory QC Checks

Laboratory performance QC is required to ensure the laboratory systems (instrumentation, samples preparation, analysis, data reduction, etc.) are operating within acceptable QC guidelines during data generation as required to meet method requirements or the client's objectives. Determination of the validity of sample results is based on the acceptance criteria being met by the control samples. The acceptance criteria for each type of control samples are defined in the appropriate SOP. These acceptance criteria are per method requirements or calculated annually from historical data.

Laboratory QC samples consist of method blanks, instrument blanks, laboratory control samples and calibration verification samples. In addition to laboratory performance QC, matrix-specific QC is utilized to determine the effect of the sample matrix on the data being generated. Typically, this includes matrix spikes, matrix spike duplicates, sample duplicates and the use of surrogate compounds. A brief description of these QC checks is presented below.

Batch

Environmental samples which are prepared or analyzed together with the same process and personnel, using the same lot(s) of reagents. A ***preparation batch*** is composed of one to 20 environmental samples (may be more for Nutrients) of the same matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An ***analytical batch*** is composed of prepared environmental samples (extracts, digestates or concentrates) or those samples not requiring preparation, which are analyzed together as a group using the same calibration curve or factor. An analytical batch can include samples originating from various environmental matrices and can exceed 20 samples.

Blind sample

A blind sample is a sample submitted for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process.

Calibration

To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

Initial Calibration Verification Standard

An Initial Calibration Verification Standard (ICV) is a second source standard analyzed immediately following calibration and indicates whether sample analysis can proceed. Generally, there should be less than a five to ten percent difference between the calculated and the true value, depending on the method.

Continuing Calibration Verification Standard (equivalent to Calibration Check Standard or CCC)

A Continuing Calibration Verification Standard (CCV) also referred to as CV, is an analytical standard that is reanalyzed with test samples to verify calibration of the analytical system. CCVs are usually mid-range standards that are analyzed at the beginning and end of an analytical run and after every 10 or 20 samples for large analytical runs. The acceptance criterion for the CCV varies per method and is defined in the analytical SOP. If the calculated value is greater than the criteria specified in the method or SOP, the measurement system is no longer in calibration and samples need to be reanalyzed.

Confirmation

A confirmation shall be performed to verify the compound identification when positive results are detected in a sample from a location that has not been previously tested by the laboratory. Such confirmations shall be performed on organic tests such as pesticides, acid herbicides or when recommended by the analytical test method except when the analysis involves the use of a mass spectrometer.

When samples results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results should be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the results using the formula described in Section 12 where R1 and R2 are the results for the two columns and the vertical bars in the equation indicate the absolute value of the difference. Therefore, RPD is always a positive value.

If one result is significantly higher (e.g., >40%), check the chromatograms of both sample and standards to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or analyst) during peak integration.

If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result(s) and qualify the result(s) as estimated. This approach is taken (based on a recommendation made by EPA Region IV) because the higher concentration always has a higher likelihood of having been influenced by interferences. The data user should be advised of the disparity between the results of the two columns. The analyst will use his/her best professional judgment as to when to report the compound(s) as non-detect.

Method Blank (equivalent to a laboratory reagent blank or LRB)

The method blank is a QC sample that consists of all reagents specific to the method and is carried through every aspect of the procedure, including preparation, cleanup and analysis. The method blank is used to identify any interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Potential sources of contamination include solvent, reagents, glassware, other sample processing hardware, or the laboratory environment. In general, the method blank is a volume of deionized laboratory water for inorganic water samples, well water for organic water samples, or Ottawa sand for soil/sediment samples, that is processed as a sample. The volume or weight of the method blank must be approximately equal to the sample volume or sample weight processed. A method blank shall be prepared with each group of samples processed. Method blanks are also referred to as laboratory reagent blanks.

The source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem if the blank contamination exceeds a concentration greater than 1/10 of the measured concentration of any sample in the associated sample batch. Any sample associated with the contaminated blank shall be reprocessed for analysis or the results reported with the appropriate data qualifier code.

Instrument Blank

The instrument blank is an unprocessed aliquot of reagent water used to monitor the contamination of the analytical system at the instrument. System contamination may lead to the reporting of elevated analyte concentrations or false positive data. The instrument blank does not undergo the entire analytical process and generally consist of an aliquot of the same reagent(s) used for a sample dilution. Instrument blanks are also referred to as continuing calibration blanks.

Laboratory control sample (equivalent to a laboratory fortified blank or LFB)

A laboratory control sample (LCS) is a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The fortified blank is analyzed exactly like a sample. Fortified blanks are used to obtain a recovery from the solution used to spike a matrix spike sample. Results are used to validate or reject matrix spike recovery results. A low or high sample matrix spike recovery can be justified if the fortified blank also shows a similar

bias and all other QC data is acceptable. This may indicate analyst error in the preparation of the spiking solution. If sample recovery results are outside control limits and the fortified blank recovery results are acceptable it is reasonable to assume a sample matrix effect is biasing results. Analysts may attempt to eliminate the interference or else flag the sample results with a sample qualifier code.

Matrix Spike (equivalent to Laboratory Fortified Matrix or LFM)

A matrix spike (MS) is an environmental sample to which known concentrations of target analytes have been added. MS samples are analyzed to evaluate the effect of the sample matrix on the analytical methodology. MS samples are generated by taking a separate aliquot of an actual client sample and spiking it with the selected target analyte(s) prior to sample extraction. The MS sample then undergoes the same extraction and analytical procedures as the unfortified client sample. Due to the potential variability of the matrix of each sample these results may have immediate bearing only on the specific sample spiked and not on all samples in the QC batch.

If the mandated or requested test method does not specify the spiking components, the laboratory shall spike all reportable components to be reported in the LCS and MS. However, in cases where the components interfere with accurate assessment (such as simultaneously spiking chlordane, toxaphene and PCBs in Method 608), the test method has an extremely long list of components or components are incompatible, a representative number (at a minimum 10%) of the listed components may be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses, permit specified analytes and other client requested components. However, the laboratory will make every attempt to ensure that all reported components are used in the spike mixture within a two-year time period.

Matrix Spike Duplicate (equivalent to Laboratory Fortified Matrix Duplicate or LFMD)

A matrix spike duplicate (MSD) is a second aliquot of a sample that is spiked with the selected target analyte(s) and analyzed with the associated sample and MS sample. The results of the MS and MSD are used together to determine the effect of a matrix on the accuracy and precision of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results may have immediate bearing only on the specific sample spiked and not all samples in the QC batch.

Sample Duplicate

A sample duplicate is a second aliquot of an environmental sample taken from the same sample container that is processed identically with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The results are compared to determine the sample homogeneity and the precision of the analytical process.

Surrogates

Surrogates are organic compounds that are similar in chemical composition and behavior to the target analytes but that are not normally found in environmental samples. Surrogate compounds must be added to all samples, standards, and blanks for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. Poor surrogate recovery may indicate a problem with sample composition and shall be reported to the client whose sample produced poor recovery.

Tuning Solution

Tuning solutions are used to determine acceptable instrument performance prior to calibration and sample analysis for GC/MS analysis.

Post-Digestion Spike

A recommended quality control sample whenever a new or unusual sample matrix is encountered. The spike is added to the sample after digestion. It is a test for matrix interference (positive or negative bias). The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrument detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

Interference Check Sample

An interference check sample (ICS) is a solution containing known concentrations of both interfering and analyte elements. Analysis of this sample can be used to verify background and inter-element correction factors.

Internal Standards

An internal standard (IS) is a compound or element with similar chemical characteristics and behavior in the analysis process of the target analytes, but is not normally found in environmental samples. The internal standard is usually added after sample preparation. The primary function of the internal standard is quantitation; however, it also provides a short-term indication of instrument performance. For isotope dilution methods, internal standards are added during sample preparation and are used for quantitation.

Quality Control Check Samples

In general, these samples are prepared similarly to the LCS, except that the reagent water is spiked with all compounds of interest. It must be from an independent source from the calibration standards. The standard is generally required in 40 CFR Part 136 methods (e.g., 624) due to the long list of analytes and the risk that the spiked sample may have some analytes outside of control limits. Note the required concentration of the standard as described within the published method or laboratory SOP.

Range

The range is the difference between the minimum and the maximum of a set of values.

11.2 Methods of Calculations for QC

11.2.1 Generating control limits for Precision and Accuracy

Precision is estimated from the relative percent difference (RPD) of the concentrations (not the recoveries) measured for matrix spike/matrix spike duplicate pairs, or for duplicate analyses of unspiked samples. For each matrix spike/matrix spike duplicate or sample and sample duplicate analyzed, calculate the relative percent difference, as described in Section 12.1.4.4 (Data Reduction, Verification and Reporting). If calculated from three or more replicates, relative standard deviation (RSD) is calculated as described in Section 9.3.3.3, rather than RPD.

Note: Range is a better measurement of precision than RPD as analytical results approach the MDL (20 x the MDL is a reasonable figure). This is especially important for those analyses that do not lend themselves to spiking (e.g., BOD and solids). For each sample and sample duplicate using range for precision, calculate range as follows:

$$Range = \left|C_{(1)} - C_{(2)}\right|$$

Where:
$C_{(1)}$ = Measured concentration of the first sample aliquot
$C_{(2)}$ = Measured concentration of the second sample aliquot

Calculate the average (p) and the standard deviation (s) for each of the duplicated compounds after analysis of 20-30 duplicate samples of the same matrix.

Calculate control and warning limits for each compound (since RPD or range are expressed as a positive number, there can be no lower control limit, as that value would be a negative number), as follows:

Control limit = p + 3s
Warning limit = p + 2s

Control limits approximate a 99% confidence interval around the mean, while warning limits approximate a 95% confidence interval. Statistically, 68% of all results should fall within one standard deviation of the mean. Statistically, seven consecutive results on either side of the mean indicate an anomaly that should be

corrected, while three consecutive results exceeding warning limits also indicate an event that should be investigated.

Any matrix spike, surrogate, or laboratory control sample (LCS) result outside of the control limits requires evaluation by the supervisor. Such actions should begin with a comparison of the results from the sample or matrix spike sample with the LCS results. If the recoveries of the analytes in the LCS are outside of the control limits, then the problem may lie with the application of the extraction or cleanup procedures applied to the sample matrix or with the chromatographic procedures. Once the problem has been identified and addressed, corrective action may include the re-analysis of sample, or the extraction and analysis of new sample aliquots, including new matrix spike sample and LCS. When the LCS results are within the control limits, the problem may either be related to the specific sample matrix or to an inappropriate choice of extraction, cleanup, and determinative methods. For a further discussion of corrective action, see Section 13.

Control (acceptance) limits and warning limits are printed and updated at the **least,** annually. Once limits are updated, the new limits are posted in the laboratory (dated and approved by the QA Officer) and entered into a master log. The QA Officer maintains an archive of all limits used within the laboratory with the start and ending effective dates. The control and warning limits used to evaluate sample results are those that are in place at the time of sample analysis.

For methods and matrices with very limited data (e.g., unusual matrices not analyzed often), interim limits are established using available data or by analogy to similar methods or matrices.

Results used to develop acceptance criteria must meet all other QC criteria associated with the determinative method. For instance, matrix spike recoveries from a GC/MS procedure are generated from samples analyzed only after a valid GC/MS tune and a valid initial calibration that includes the matrix spike compounds. Another example is that analytes in GC methods must fall within the established retention time windows in order to be used to develop acceptance criteria.

It is advisable to consider the effects of the spiking concentration on matrix spike control limits, and to avoid censoring of data. The acceptance criteria for matrix spike recovery and precision are often a function of the spike concentration used. Therefore, caution must be used when pooling matrix spike/matrix spike duplicate data to generate control limits. Not only should the results all be from a similar matrix, but the spiking levels should also be approximately the same (within a factor of 2). Similarly, the matrix spike and surrogate results should all be generated using the same set of extraction, cleanup and analysis techniques. For example, results from solid samples extracted by ultrasonic extraction are not mixed with those extracted by Soxhlet.

Another common misstep in developing acceptance criteria is to discard data that do not meet a preconceived notion of acceptable performance. This results in a censored data set, which, when used to develop acceptance criteria will lead to unrealistically narrow criteria. Remember that for a 95% confidence interval, 1 out of every 20 observations likely will still fall outside the limits. While professional judgement is important in evaluating data to be used to develop acceptance criteria, specific results are not discarded simply because they do not meet one's expectations. Rather, a statistical test for outlier values is employed (see Section 11.3).

In-house QC limits must be examined for reasonableness. Poor recoveries should not be legitimized due to the incorrect choice of methods or spiking levels. In-house limits are important when considering the objectives of specific analyses. For example, recovery limits that include allowance for a relatively high positive bias (e.g., 70-170%) may be appropriate for determining that an analyte is <u>not</u> present in a sample. However, they would be less appropriate for the analysis of samples near but below a regulatory limit, because of the potential high bias.

It may be useful to compare QC limits generated in the laboratory to the performance data that may be listed in specific determinative methods. However, be aware that performance data generated from multiple laboratory data tend to be significantly wider than those generated from single laboratory data. In addition, comparisons between in-house limits and those from other sources should generally focus more on the

accuracy (recovery) limits of single analyses rather than the precision limits. For example, a mean recovery closer to 100% is generally preferred, even if the ±3 standard deviation range is slightly wider, because those limits indicate that the result is likely closer to the "true value". In contrast, the precision range provides an indication of the results that might be expected from repeated analyses of the same sample.

11.2.2 Standard Deviation and Control Limits

Historical data that the laboratory generates are used to calculate in-house control limits for matrix spike recoveries, surrogate recoveries and laboratory control sample recoveries. The development of in-house control limits and the use of control charts or similar procedures to track laboratory performance are important.

Accuracy is estimated from the recovery of spike analytes from the matrix of interest. For each matrix spike sample, calculate the percent recovery of each matrix spike compound added to the sample, as described in Section 12.1.4.3 (Data Reduction, Verification and Reporting).

For each collected sample, calculate the percent recovery of each surrogate, as follows:

$$Recovery\ (\%) = (\frac{Conc.\ (or\ amt.)found}{Conc.\ \ (or\ amt.)added}) * 100$$

Calculate the average percent recovery (p) and the standard deviation (s) for each of the matrix spike compounds after analysis of 20-30 matrix spike sample of the same matrix. Calculate the average percent recovery (p) and the standard deviation (s) for each of the surrogates after analysis of 20-30 collected sample of the same matrix, in a similar fashion.

Calculate upper and lower control limit for each matrix spike or surrogate compound, as follows:

Upper control limit = p + 3s
Lower control limit = p - 3s

Calculate warning limits as:

Upper control limit = p +2s
Lower control limit = p - 2s

In general, the laboratory utilizes method or laboratory defined warning and control limits for reporting data (i.e., statutory control limits). Those statutory limits may be modified utilizing statistical information collected over time. The precision and recovery data are used for the diagnosis of analytical problems. For laboratory parameters, calculated statistical control limits are used as criteria to accept or reject data only if they are more stringent than the criteria in Table 5.1.

The formulae used for the calculation of standard deviation, mean, upper and lower control and warning limits are shown below. (Reference: Chapter 6 of "*Handbook for Analytical Quality Control in Water and Wastewater Laboratories" - EPA 600/4-79-019, March 1979*).

a. Standard deviations are calculated based on the formula:

$$Sp = \sqrt{[\sum_{i=1}^{n} P_i^2 - (\sum_{i=1}^{n} P_i)^2 / n] / n - 1}$$

Where:
Sp = standard deviation of the population
n = total number of points in the population
P_i = the value for each point

b. The mean is calculated as the average of all points:

$$\overline{P} = \frac{\sum_{i=1}^{n} Pi}{n}$$

c. For recovery, the upper and lower control limits are based on a 99% confidence level.

$$UCL = P + t_{(0.99)}Sp$$

$$LCL = P - t_{(0.99)}Sp$$

d. The upper and lower warning limits for recovery are based on a 95% confidence level.

$$UWL = P + t_{(0.95)}Sp$$

$$LWL = P - t_{(0.95)}Sp$$

Where $t_{(0.99)}$ and $t_{(0.95)}$ are Student's t factors for 99% and 95% confidence, respectively.

Because levels of statistical confidence vary with sample size, a fixed level of statistical confidence is employed that approximates 2 and 3 standard deviations. Those control limits are based on requirements specified in various EPA methods and in EPA's 'Handbook for Analytical Quality Control in Water and Wastewater Laboratories'. The statistical program utilizes a Student's t table, setting warning limits at 95% confidence and control limits at 99% confidence. Those Student's t factors correspond approximately to 2 and 3 standard deviations for 7 collected data points. The advantage of using Student's t factors is that control limits are based on known confidence limits regardless of the number of data points in the population.

e. For precision on duplicate samples, the upper warning and control limits are based on a 95% and 99%confidence level, respectively.

$$UWL = D_3P$$

$$UCL = D_4P$$

Where D_3 and D_4 are Shewhart factors representing 95% and 99% confidence limits for pairs of duplicates and P is the mean for the population of precision values (as %RPD measurements).

11.3 Statistical Outlier Tests

It is important to exclude extreme measurements from a data set to eliminate bias in statistical evaluations such as control limit calculation. Extreme or atypical values are often referred to as outliers because of their location outside the normal distribution for a particular data set. When data follow a Gaussian distribution, certain statistical assumptions can be made about the data:

- about 68% of the measurements will be within one standard deviation of the mean;
- about 95% of the measurements will be within two standard deviations of the mean; and
- about 99% of all measurements will be within three standard deviations of the mean.

Outliers may be rejected outright only when they are caused by a known or demonstrated physical reason, such as sample spillage, contamination, mechanical failure or improper calibration. Data points, which appear to deviate from the expected sample distribution for no known physical reason, must be verified as outliers using statistical criteria.

11.3.1 Z-Score

Z-scores can be calculated for large sample sizes (greater than 30 data points), and thus are useful to determine if a value should be excluded from a calculation of control limits. A Z-score of greater than 4 is an indication that the data point in question is an outlier. The Z-score is calculated as follows:

$$Z = \frac{|X - X_{bar}|}{S}$$

Where:
Z = Z-score
X= the measurement in question
X_{bar} = the mean of the measurements
S = the standard deviation of the measurement

Look up the critical value of Z in Table 11.1 below, where N is the number of values in the data set. If the calculated Z value is greater than the tabulated value, then the P value is <0.05. This means that there is less than a 5% chance that you'd encounter an outlier.

11.3.2 Grubbs' T test

The Grubbs' T test is an objective test for determining whether a point is an outlier in a smaller data set (less than 20 data points). The Grubbs' T value is calculated as follows:

$$T = \frac{|X_q - X_{bar}|}{S}$$

Where:
T = Grubbs' T value
X_q = the measurement in question (the data point furthest from the mean)
X_{bar} = the mean of the measurements
S= the standard deviation of the measurement

The result of the calculation is compared against the value of T from Table 11.1, using the appropriate number of measurements and the acceptable rejection factor (the 5% rejection factor is presented here). If the Grubbs' T value is greater than the value of T from the table, the data point in question is a statistical outlier, and should be rejected from the data set.

The Grubbs' test detects one outlier at a time. This outlier is expunged from the data set and the test is iterated until no outliers are detected. However, multiple iterations change the probabilities of detection, and the test should not be used for sample sets of 6 or less since it frequently tags most of the points as outliers.

Table 11.1. Critical values for Grubb's T

Number of Data Points	Critical Value T
7	1.94
8	2.03
9	2.11
10	2.18
12	2.29
14	2.37
15	2.41
16	2.44
18	2.50
20	2.56

11.4 Method Detection Limits (MDL) and Practical Quantitation Limits (PQL)

The MDL defined below is adapted from 40 CFR Part 136, Appendix B. Similarly, the PQL is defined on the basis of this MDL study.

11.4.1 Scope and Application

The MDL is defined as the minimum concentration of an analyte that can be measured by the method with 99% confidence of its presence in the sample matrix. This procedure is designed for applicability to a wide variety of sample types ranging from reagent water spiked with the analyte, to wastewater containing analyte, to sand or other solid matrices containing the analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well-defined analytical method. It is essential that all sample-processing steps of the analytical method be included in the determination of the MDL. The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample. The MDL procedure was designed for applicability to a broad variety of physical and chemical methods, and should be performed in both aqueous and non-aqueous matrices (where samples are analyzed in both matrix types). MDLs must be determined each time there is a significant change in the test method or instrument type. A MDL study is not required for any component for which spiking solutions or quality control samples are not available, such as BOD_5, $CBOD_5$, TS, TSS, TDS, coliform, chlorophyll *a*, turbidity and color.

11.4.2 Procedure

Make an estimate of the detection limit using one of the following:

- The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5.
- The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.
- That region of the standard curve where there is significant change in sensitivity, i.e., a break in the slope of the standard curve.
- Instrumental limitations.
- It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

Prepare a matrix (i.e., reagent water) that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferant concentrations are not detected at the MDL of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferant). The interferant concentration is presupposed to be normally distributed in a representative sample of a given matrix.

11.4.2.1 Matrix choice

- If the MDL is to be determined in reagent water, prepare a laboratory standard at a concentration which is at least equal to or in the same concentration range as the estimated detection limit (recommend between 1 and 5 times the estimated detection limit).
- If the MDL is to be determined in another sample matrix, analyze recommended range of one to five times the estimated detection limit. (Note: Clean sand may also be spiked to determine the MDL for solids).
  - If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.
  - If the measured level of analyte is greater than five times the estimated detection limit, there are two options.
- Obtain another sample with a lower level of analyte in the same matrix if possible.
- This sample may be used as is for determining the MDL if the spike level does not exceed 10 times the calculated MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL; hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

11.4.2.2 Analysis

It may be economically and technically desirable to evaluate the estimated MDL before proceeding with 11.4.2.2a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated MDL. To insure that the estimate for the MDL is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower MDL. The two aliquots of the sample to be used to calculate the MDL and process each through the entire method, including blank measurements as described above in 11.4.2.2a.

- If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional sample aliquots and proceed. Use all seven measurements for calculation of the MDL.
- If these measurements indicate the sample is not in correct range, re-estimate the MDL, obtain new sample as in 11.4.2.1 and repeat either 11.4.2.2a or 11.4.2.2b.

Take a minimum of seven aliquots of the sample to be used to calculate the MDL and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. Where allowed by the methods, the average blank measurement is subtracted from the respective sample measurements.

Calculate the standard deviation (s) of the replicate measurements.
Compute the MDL, as follows:

$$\mathbf{MDL = t_{(n-1,\ 1-\mu=0.99)}\ (s)}$$

Where:
MDL = the method detection limit
$T_{(n-1,\ \mu-1=0.99)}$ = the Student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (see Table 11-2).
S = standard deviation of the replicate analyses.

Table 11.2. Students' t-Values at the 99% Confidence Level

Number of replicates	Degrees of freedom (n-1)	$T_{(n-1,\ 0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
12	11	2.718
13	12	2.681
14	13	2.650
15	14	2.624
16	15	2.602
17	16	2.583
18	17	2.567
19	18	2.552
20	19	2.539

The MDL is recalculated/verified on at least an annual basis or anytime any major changes have been made to the analytical system. A processed blank sample is analyzed with each sample set.

The PQL is considered the lowest level of concentration that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. This laboratory generally sets the PQL at 3 to 5 times the MDL depending on the method of analysis and the analyte, unless otherwise specified.

11.5 MDL Reporting

The analytical method used must be specifically identified by number and method title. The date of the study, instrument ID and the name of the analyst(s) performing the analysis must be included. If the analytical method permits options that affect the MDL, these conditions must be specified with the MDL value (i.e., sample preparation methods, columns, and detectors). The sample matrix, date of calibration and the standard (ID# and concentration) used must be documented. The MDL for each analyte must be expressed in the appropriate method reporting units. Report the mean analyte level with the MDL. If a laboratory standard or a sample that contained a known amount of analyte was used for this determination, also report the mean recovery. If the level of analyte in the sample was below the determined MDL or exceeded 10 times the MDL of the analyte in reagent water, do not report a value of the MDL. MDL study will be repeated using another concentration. An example format for documenting each MDL can be found in Figure 11.1.

11.6 Blind QC Check Sample Analysis

The laboratory participates in EPA's Performance Evaluation Studies. Results of these tests are summarized and included in the laboratory's QA report.

Figure 11.1. Example MDL Reporting Format

Laboratory Name:		**Analytical Method:**	
Analyst(s) Name(s):		**SOP#:**	
Date:		**Instrument/serial #:**	
Sample Prep. Method:		**Column:**	
Sample Prep. SOP#:		**Detector:**	
Matrix:		**Cleanup/Modification:**	

Analyte	Spike conc.	Units	1	2	3	4	5	6	7	Mean Recovery %	Average Recovery X	Standard Deviations	MDL	PQL
Blank														

P=Pass F=Fail

MDL = t (n-1, 1-a = 0.99) (s)
t = Student's t values appropriate for 99% confidence level. Table of Students' t values can be found in 40 CFR Part 136, Appendix B. Student t-value used:
PQL = 3 to 5 times the calculated MDL.

Comments:

_____

_____	_____	_____
Chemist's/Technician's Name (print)	Signature	Date
_____ _____	_____	_____
Branch Manager's Name (print)	Signature	Date
_____ _____	_____	_____
Lead Chemist's Name (print)	Signature	Date
_____ _____	_____	_____
Quality Assurance Officer's Name (print)	Signature	Date

12.0 Data Reduction, Verification and Reporting

In order to provide complete, accurate and verifiable results, all analytical data generated by the DWR Water Sciences Section Chemistry Laboratory is recorded, reviewed, reported and archived according to Laboratory policy. Analytical areas have slightly different data reduction, validation and reporting protocols depending on the means by which the data are generated and specific method requirements. The general procedures involved in the process of data reduction, validation and reporting are explained in this section. Detailed procedures are outlined in laboratory operational or analytical SOPs.

12.1 Data Reduction

Data reduction includes all activities that convert analytical values into reportable sample concentrations of the target analyte(s). These activities may involve mathematical calculations, compound identification and summary statistics. The final results may be obtained in two ways:

1. Direct readings from the instrument; or
2. Calculations based on instrument output, readings or responses.

The Water Sciences Section Chemistry Laboratory's goal is to minimize the steps needed to transform raw data into reportable results and maximize on the number of analytical results generated by automated systems. The more automated the data reduction process, the less likely data transcription and calculations errors are to occur.

12.1.1 Manual data reduction

Manual data reduction refers to those activities in which analytical output is converted to sample concentrations by calculations performed manually or by validated computer applications.

- During the manual data reduction process, analysts will:
- Assure that all data are correctly transcribed into worksheets, forms or computer application;
- Keep raw data as part of the analysis records (e.g., tabulated reports, chromatograms, etc.)
- Select the appropriate, method-specified formulae for calculating results. The formulae used are written in the standard operating procedures for each method
- Proofread computer-generated reports to ensure that the raw data manually entered into the computer application was entered correctly.
- Record appropriate and accurate information concerning sample identification, operating conditions, etc.

The Water Sciences Section Chemistry Laboratory retains documentation of all computer applications used for this purpose, including the mathematical formulae used to calculate sample concentrations. If such information is not available, or can not be obtained from the code, the application is validated by comparing the results of the application with the results of manual calculations. A record of this verification is maintained in the analytical unit. Data is to be retained at laboratory for five years and then archived downtown for an additional five years. Please note DENR data retention policy in appendix IV.

All raw data output (i.e., strip charts, tabular printouts, etc.) must be identified with the following information (where applicable):

- Date of analysis
- Sample ID numbers
- Analyst or operator
- Type of analysis
- Instrument operating conditions
- Detector
- Column
- Instrument configuration

12.1.2 Computer data reduction

Computer data reduction refers to those activities in which analytical acquisition and initial calculations are performed automatically by validated computer applications.

When computer data reduction is performed, the analysts will (as is appropriate to the method used):

- Ensure that all variables required for final calculations (sample amount, dilution factor, extract volume, percent solids, surrogate amount, etc.) are entered accurately;
- Properly interpret the computer output in terms of correctly identified components, positive or negative identifications and appropriate confirmatory measures;
- Record appropriate and accurate information concerning sample identification, operating conditions, etc.;
- Calculate surrogate recoveries and verify that internal standard responses are acceptable;
- Verify that target compounds analyzed by chromatographic methods are within the appropriate retention time or relative retention time windows and that additional confirmation is initiated as needed.

Raw data files are assigned a unique filename by the analyst performing the analyses. In some instances, the computer performs the filename assignment using rules that ensure that filenames will not be repeated (i.e., a queue number). In such cases, a cross-reference index or log is maintained to identify the computer data files with sample ID numbers. Additional information that should be entered into the data file records are date of analysis, analysis type and analyst initials. Cross-referenced auxiliary records may be required to identify instrument operating conditions. Many analytical instruments are interfaced with computers or integrators that automatically evaluate, identify and calculate final values. The results are printed in combinations of graphic (e.g., chromatograms) and tabular forms. As with manual data reduction, the Section must be aware and should have on file a record of the mathematical formulae or algorithms that are being used by the computer. If the information is not available, the organization shall maintain records, which demonstrate that the software is providing the expected results.

12.1.3 General data reduction responsibilities

Additional data reduction responsibilities include:

- Ensuring that samples are analyzed only when the instrument is calibrated according to the method;
- Ensuring that QC results are calculated correctly, within criteria, and if not, initiating corrective actions;
- Identifying QC results for review by the responsible person(s);
- Documenting sample preparation and analysis, and the conditions under which they were performed, inappropriate logbooks or on appropriate benchsheets;
- Ensuring that the laboratory sample ID is directly traceable to the field sample and is correctly transcribed into all associated analytical records;
- For computer-controlled data acquisition and data reduction, the analysts are responsible for entering all the parameters needed for final result calculation correctly;
- For manual data reduction, the analysts are responsible for performing the calculations according to the method requirements;
- If the result is transcribed, the analysts are responsible for ensuring that the entry is entered correctly;
- The analysts are responsible for alerting a Supervisor about any problems that the analyst believes may affect the quality of the data.

Every instrument or method within the six analytical areas and one regional laboratory has a slightly different data reduction process depending on the way in which data are generated and the required data transformations. Most sample concentration results are read directly from instrumentation without further reduction or calculations.

Dilution factors are applied upon the dilution of samples having concentrations above the calibration range. In many cases, these are input into the instrument computer and correct results are calculated automatically. In other cases, a manual calculation may be performed (this may be done by hand or by entering the raw data result into an Excel spreadsheet programmed to perform the additional data manipulations). The Water Sciences Section calculates results according to the guidance provided in the methods cited in Section 5. Exceptions would be clearly noted in the raw data and on final reports.

Water Sciences Section Chemistry Laboratory's soil/sediment concentration results are calculated on a dry weight basis, prior to reporting, by dividing the instrument result by the fractional dry weight. Section 12.1.4 lists equations used in computer-controlled instrumentation for data reduction as well as equations used for the manual calculation of reportable concentration results.

The laboratory raw data containing the instrument-generated reports, manually calculated results, and all supporting preparation, calibration, and analytical data are retained at the individual work stations until reports are issued unless additional handling or data packaging is required. Laboratory SOPs include equations used to calculate results, the method of calculation, benchsheets used to record pertinent data for each analytical method and a description of the data reduction process. All data processed either manually or electronically is verified by a second analyst.

Analytical results are reduced to appropriate concentration units specified by the analytical method, taking into account factors such as dilution, sample weight or volume, significant figures, etc. If components of interest are detected in any quality control blank (e.g. method blanks, digestion blanks, etc.), certain methods require that the blank concentration must be reported. The blank concentration shall not be subtracted from any associated sample data. Blank correction will be applied only when required by the method/per manufacturer's indication; otherwise, it should not be performed.

It is the Water Sciences Section Chemistry Laboratory's policy to report automated peak integration results; however, manual integration is allowed if peaks are not properly integrated by the software. Improper integration includes:

- Integration of the wrong peak,
- Not finding the peak at all,
- Improper division of co-eluded peaks, and
- Improper drawing of baseline under a peak.

Manual integration is performed along the baseline or above noise level. Calculations are independently verified by appropriate laboratory staff. Manual integrations must never be used solely to meet QC criteria or as a substitute for corrective actions on the analytical system. Corrective action with regard to the instrumentation or computer software must be taken if manual integrations become common for an analysis or instrument that normally uses automated peak integration. Manual integration must be clearly identified and documented on the data report by flagging the affected analytes. The analyst must initial and date the corrected data.

For dual columns (as in gas chromatography), the default procedure is to report the lowest result between the primary and confirmation columns if the relative percent difference (%RPD) is <40%. If the %RPD exceeds 40%, the analyst evaluates the data for the presence of matrix interferences and reports the result that is most appropriate for that sample and flags the results as estimated to note the discrepancy.

Where there are cases in which the results from spiked samples suggest interferences, attempts are made to remove the interferences, or alternate analytical procedures are used. If the interference problem cannot be resolved, the data is flagged and an explanation included on a SAR form and in the sample comments of the final report. Sample comments are representative of SAR information.

12.1.4 Formulae and Calculations

The final results of each test shall be calculated by the formula specified in the analytical method that is being used. If the formulas outlined in this section are not used, the correct formula can be found in the appropriate method SOP.

12.1.4.1 The analyte concentration in a sample analyzed using external standard calibration can be determined by:

$$Concentration\ (ppb) = \frac{(A_s)(V_t)(D)}{(avgCF)(V_i)(S)}$$

where:
A_s is the area of the peak for the analyte in the sample
V_t is the total volume of the extract in µl (for purge and trap analysis V_t=1)
D is the dilution factor (if no dilution is performed, D=1)
avgCF is the mean calibration factor from the initial calibration in area/ng
V_i is the volume of the extract injected in µl (for purge and trap analysis V_i = 1)
S is the sample volume or mass (in mL or g) extracted or purged

12.1.4.2 The analyte concentration in a sample analyzed using internal standard calibration can be determined by:

$$Concentration\ (ppb) = \frac{(A_s)(C_{is})(V_t)(D)}{(A_{is})(avgRF)(S)}$$

where:
A_s is the area of the peak for the analyte in the sample
C_{is} is the concentration of the internal standard
V_t is the total volume of the extract in mL (for purge and trap analysis V_t=1)
D is the dilution factor (if not dilution is performed D= 1)
A_{is} is the area of the internal standard
Avg RF is the mean response factor form the initial calibration
S is the sample volume or mass (in L or kg) extracted or purged

12.1.4.3 Calculated values for spiked samples, duplicate analyses, and reference standards are compared with quality control limits to determine data validity. Recovery of any spiked analyte (including surrogate compounds) is calculated as:

$$\%Recovery = \left(\frac{C_s - C_u}{C_n}\right)100$$

where:
C_s is the measured concentration of the analyte or surrogate
C_u is the concentration of the unspiked sample (for LCS and surrogate recoveries C_u = 0)
C_n is the true value or known concentration of the analyte or surrogate.

12.1.4.4 The precision of duplicate analyses is determined from the relative percent difference (RPD) calculated by:

$$RPD(\%) = \left(\frac{2|R_1 - R_2|}{R_1 + R_2}\right)100$$

where:
R_1 is the measured concentration of one replicate
R_2 is the measured concentration of the second replicate

12.1.4.5 Relative Standard Deviation (RSD) is computed from the standard deviation and mean recovery when the standard deviation is derived from multiple recovery results:

$$RSD(\%) = \left(\frac{Standard\ Deviation}{Mean\ Recovery}\right)100$$

12.1.4.6 Sample and QC result calculations are reduced as follows:

A. Results from analyzed sample extracts or digestates are processed manually by the analytical instruments' PC-based data systems or by laboratory chromatography software, based on the method protocols discussed in Sections 5 and 9. These raw sample results are manually calculated or manually/electronically downloaded from the analytical instrument to the appropriate computer application.

B. Sample results and QC results are linked together by date of analysis and assigned lab numbers, so sample prep and analysis batches are always identified with their associated QC. Using pertinent sample prep/analysis data (e.g., amount of sample digested or extracted, final digestate or extract volume, dilution factors, spiking level/solution used, etc.), calculations are either performed manually or by an appropriate computer application. Examples of typical water and sediment calculations performed follow:

Concentration in µg/L (for water samples) =

$$\frac{\text{Final extract or digestate conc. (µg/mL) x Final extract or digestate volume (mL)}}{\text{Initial Sample Volume Extracted or Digested (L)}}$$

Concentration in µg/kg (for sediment samples) =

$$\frac{\text{Final extract or digestate conc. (µg/mL) x Final extract or digestate volume (mL)}}{\text{Initial Sample Weight Extracted or Digested (kg) x Dry Weight Correction Factor}}$$

C. The resulting sample and associated QC results are reviewed by the chemist, results deemed acceptable, are entered into DWR LABWORKS™ database. Current acceptance criteria (warning and control limits) for each QC element are stored within an Excel spreadsheet or posted in the analytical unit. If QC results are outside of the current control limits, data is flagged with the appropriate qualifier code. The analysis data is fully reviewed to determine if sample contamination or matrix problems exist. The associated sample batch may then be re-submitted for re-digestion/re-extraction or re-analysis. If there is still a problem with the quality of the data, in-depth investigation into the method in question is conducted until the problem is resolved. The data may be rejected or reported with qualification if the problem cannot be resolved immediately.

12.1.5 Corrections

Entries in records shall not be obliterated by methods such as erasures, liquid paper, overwritten files or markings. All corrections to record-keeping shall be made by one line marked through the error leaving the original record visible. The individual making the correction shall sign (or initial) and date the correction. These criteria shall also apply to electronically maintained records.

12.1.6 Significant Figures

Every measurement has a degree of uncertainty associated with it. The uncertainty derives from the limitations of the measuring device and from the skill with which it is used. The accuracy of a measurement is expressed by the number of significant digits (or significant figures) written when the measurement is reported. All digits in a reported result are expected to be known definitely, except for the last digit, which may be in doubt (i.e., has an uncertainty of ± 1 unit). Such a number is said to contain only significant figures.

12.1.6.1 Significant Figure Rules

There are several rules for determining the number of significant digits (or significant figures) in a measurement. In general significant figures are determined starting with the leftmost digit.

1. Non-zero digits are always significant.
2. All zeros between other significant digits are significant.
3. The number of significant figures is determined starting with the leftmost non-zero digit. The leftmost non-zero digit is sometimes called the most significant digit or the most significant figure. For example, in the number 0.004205 the '4' is the most significant figure. The left-hand '0's are not significant. The zero between the '2' and the '5' is significant.
4. The rightmost digit of a decimal number is the least significant digit or least significant figure. Another way to look at the least significant figure is to consider it to be the rightmost digit when the number is written in scientific notation. Least significant figures are still significant. In the number 0.004205 (which may be written as 4.205×10^{-3}), the '5' is the least significant figure. In the number 43.120 (which may be written as 4.3210×10^{1}), the '0' is the least significant figure.
5. If no decimal point is present, the rightmost non-zero digit is the least significant figure. In the number 5800, the least significant figure is '8'.

12.1.6.2 Precision and Uncertainty in Calculations

Measured quantities are often used in calculations. The precision of the calculation is limited by the precision of the measurements on which it is based.

Addition and Subtraction

When measured quantities are used in addition or subtraction, the uncertainty is determined by the absolute uncertainty in the least precise measurement (not by the number of significant figures). Sometimes this is considered to be the number of digits after the decimal point.

Example:
32.01 grams
5.325 grams
12 grams

Added together, you will get 49.335 grams, but the sum should be reported as '49 grams'.

Multiplication and Division

When experimental quantities are multiplied or divided, the number of significant figures in the result is the same as that in the quantity with the smallest number of significant figures. If, for example, a density calculation is made in which 25.624 grams is divided by 25 mL, the density should be reported as 1.0 g/mL, not as 1.0000 g/mL or 1.000 g/mL.

When doing several calculations, carry out all of the calculations to at least one more significant figure than you need, then round the final result.

12.1.6.3 Losing Significant Figures

Sometimes significant figures are 'lost' while performing calculations. For example, if the mass of a filter is found to be 53.110 g, add residue to the filter and find the mass of the filter plus residue to be 53.987 g, the mass of the residue is 53.987-53.110 g = 0.877 g The final value only has three significant figures, even though each mass measurement contained 5 significant figures.

12.1.6.4 Exact Numbers

Sometimes numbers used in a calculation are exact rather than approximate. This is true when using defined quantities, including many conversion factors, and when using pure numbers. Pure or defined numbers do not affect the accuracy of a calculation. These may be thought of as having an infinite number of significant figures. Pure numbers are easy to spot, because they have no units. Defined values or conversion factors, like measured values, may have units.

Example:
To calculate the average of three measured titration volumes: 30.1 ml, 25.2 ml, 31.3 ml; calculate as follows: (30.1 + 25.2 + 31.3)/3 = 86.6/3 = 28.87 = 28.9 ml. There are three significant figures in the volumes; even though you are dividing the sum by a single digit, the three significant figures should be retained in the calculation.

12.1.7 Rounding

Whenever data is reduced using computer applications, the rounding rules used are those provided with the operating software. The final result should be rounded off to an appropriate number of significant figures (typically 2 significant figures). When manual calculations are performed, the following rounding rules are followed:

- If the digit to be dropped is less than 5, do not change the last digit to be retained (e.g., 2.23 rounds off to 2.2).
- If the digit to be dropped is greater than 5, increase the last digit to be retained by one (e.g., 2.26 rounds to 2.3).
- If the digit to be dropped is equal to 5, increase the last digit to be retained by one if it is odd (e.g., 2.35 rounds to 2.4, or do not change the last digit to be retained if it is even (e.g., 2.45 rounds to 2.4).

As a general rule, the results should be converted to the reporting units presented in Section 12.1.8. Other reporting conventions (i.e., wet weight instead of dry weight) should be clearly identified on the final reports with appropriate justification.

12.1.8 Reporting Units

The reporting units listed below are used for results unless otherwise requested by the client. Solid matrices are reported as dry weight unless otherwise requested.

Parameter	Water	Soil
Metals (except as noted below)	µg/L	mg/Kg
Ca, Mg, Na, K	mg/L	
Hg 1631 low level	ng/L	
Purgeable Organic Compounds (except as noted below)	µg/L	µg/Kg
TPH - GRO	mg/L	mg/Kg
Extractable Organic Compounds (except as noted below)	µg/L	µg/Kg
TPH - DRO	mg/L	mg/Kg
Inorganic/Microbiology Parameters (except as noted below)	mg/L	mg/Kg
Specific Conductance	µmhos/cm@ 25ºC	
Turbidity	NTU	
Coliform, MF	Colony/100 ml	
Coliform, MPN	MPN/100 ml	
Color, PtCo	Color units (c.u.)	
Color, ADMI	Color units (c.u.)	
Boron	µg/L	
Total Phenol	µg/L	
Hexavalent Chromium	µg/L	
Chlorophyll *a*	µg/L	

12.2 Data Verification

Data verification or review is the routine laboratory process through which proper quantification, recording, transcription, and calculations are confirmed. It also confirms that the data is reasonable and complete. The process should be such that errors are minimized and that corrective action steps are taken and documented when errors are detected. The objective of data verification is to provide results of verifiable and acceptable quality whose validity is not jeopardized. The data verification process ensures that:

- The correct samples are reported;
- There were no systematic errors in calculating final results;
- Samples were analyzed within calibration and the required holding times;
- The QC elements monitored were within known acceptance limits.

Each analyst or technician is responsible for determining that the results of each analytical determination have all associated QC measurements (completeness) and that the acceptance criteria are met and documented according to protocol (correctness). The analyst or technician is responsible for checking calculations, completing sample preparation, calibration, analysis, standard and instrument logs. Each analyst, peer reviewer or supervisor is responsible for reviewing this work for completion and correctness prior to authorizing the individual results for release. This includes checking for appropriate flagging of final results. Any discrepancy or inconsistency will initiate a recheck of data or reanalysis of the sample(s).

The data verification process includes four steps: initial, secondary, and final review and release authorization.

12.2.1 Initial Review

Raw data is converted to reportable data and transcribed from benchsheets or instrument printouts onto standardized laboratory parameter spreadsheets by the analyst performing the test. The analyst performs the initial review of the data and data result entry. The analyst is responsible for verifying the correctness of the data entered into the DWR LABWORKS™ system. In some cases; such as organics, the data is not entered until all confirmations are complete. This initial review includes, but is not limited to, verifying that quality control indicators meet criteria, calibration criteria are met, appropriate detection limits were used, data was reduced correctly and that any corrective action was documented properly. The primary reviewer is responsible for verifying any documentation associated with the data, completing all records associated with the process, and completing sample anomaly reports as required. The analyst is responsible for assembling a data package containing all relevant raw data needed for data interpretation. This may include: benchsheets, instrument printouts such as quantitation reports, integrator peak area/height and retention time reports, chromatograms, and diagnostic reports. The analyst must perform primary review on 100% of the data generated.

12.2.2 Secondary Review

A party other than the analyst generating the data (e.g., a peer within the same analytical area) is responsible for a secondary review of the data. This step is intended as a verification of the primary review. Secondary review focuses on laboratory data entries and calculations for errors and mistakes, calibration criteria, quality control indicators, compound identification, results expression, reporting limits, holding times, sample and standard preparation logs, data transcription and documentation. All data are verified. If problems exist during this review, the data is returned to the primary analyst and a 100% review is done and corrective action is performed as appropriate. Once the data is checked and deemed acceptable for reporting, the secondary reviewer dates and initials the quality control section on bench worksheets or on the cover page of computer-generated reports and submits the data to the supervisor or supervisor designee for final review.

Specific checks required of the secondary reviewer are summarized in Figures 12.1 and 12.2.

12.2.3 Final Review

Final review must be performed prior to committing the data results to the DWR LABWORKS™ LIMS database by an individual familiar with it, but not involved in the original data reduction process (e.g., peer, supervisor or branch manager). The process includes, but is not limited to, verifying that chemical relationships are evaluated, sample ID numbers are correct, tests have been performed within the appropriate holding times, all precision and accuracy requirements are addressed, data transcription and data entry were performed correctly, narratives are present, flags are appropriate, SARs or sample comments on final report are attached, and project specific requirements are met.

Data found to be of doubtful quality by the analyst, through internal audits or arising from customer concerns must be reviewed by a supervisor or the QA/QC Coordinator using the procedures outlined in Section 13.

When all results for a sample have been entered into the database, the results are printed from the DWR LABWORKS™ system into a final report. The hard copy report is then checked for data entry errors by a second analyst. The report is then sent to the supervisors for release authorization.

The laboratory QA/QC coordinator reviews random final printed reports quarterly for correctness of protocol of signatures, data and sample log in entries.

12.2.4 Release Authorization

This review ensures that client requirements have been met and that the final report has been properly completed. The process includes, but is not limited to, verifying that chemical relationships are evaluated, sample ID numbers are correct, tests have been performed within the appropriate holding times, the results

are relevant to historical values, project-specific requirements have been met, and the chain of custody was maintained. This action authorizes transmittal of the final report to the client.

Figure 12.2 is a flow chart of the analytical data review and reporting process.

12.3 Reporting

Each supervisor is responsible for authorizing the individual analysis results for release. After all the sample results are authorized, the Processing Assistant uses the DWR LABWORKS™ LIMS to generate final reports in electronic and hard copy format with the appended organics report (when applicable), and any associated anomaly reports which detail the reason data was qualified. The completed report package is sent to the Environmental Program Supervisors, Unit Supervisor, and Supervisor designee for release authorization.

The Environmental Program Supervisor, Unit supervisors or program supervisor designee certify the hard copy reports by reviewing, dating and initialing. One report is retained with the original fieldsheets at the Water Sciences Section Chemistry Laboratory. The other report is mailed with copies of the fieldsheets to some clients. The report is accessible to end data uses once the report is released to the client. Some client access the final report in LABWORKS™ instead of receiving a hardcopy. All final sample results are archived in DWR LABWORKS™ LIMS databases and can be retrieved in the future if necessary.

12.3.1 Data Qualifier Codes

Data qualifier codes are used on reports as needed to inform the client of any additional information that might aid in the interpretation of the data. The data flagging system incorporates data qualifiers which are similar to flags specified in the Contract Laboratory Program protocols, and STORET, as well as additional flags used to help explain batch specific events. See Appendix II for qualifier codes and their definitions along with supporting information.

The decision to qualify a result on these factors is at the discretion of the authorizing supervisor and must comply with Water Sciences Section Chemistry Laboratory Standard Operating Procedures.

12.3.2 Report Format and Contents

Data is transmitted to laboratory data users in two ways: paper reports for each sample and by electronic read-only access. Final reports for test data are issued after all internal review has been completed. Electronic transfer of data is an option available to laboratory data users that have access to the laboratory network.

Analytical results are issued in a format that mimics the sample submission fieldsheets in the case of inorganics. Since organic parameters are multi-analyte, a separate report is attached to this report. The final reports are printed, reviewed and signed by a supervisor or their designee. Persons designated to sign reports include the Section Chief, Branch Supervisors, Unit Supervisors, and the QA/QC Officer.

An example report can be found in Figure 12.1. At a minimum, the following information must be included on all reports:

- Name of laboratory;
- Unique identification of the report (sample ID#) and of each page and the total number of pages;
- Name of the person or entity to report the results to;
- Date received;
- Date reported;
- Sample priority;
- Sample results with units of measurement;
- Relevant SCUR/SAR forms;
- Authorization signature/initials and date.

12.3.3 Corrected Reports

Occasionally a report must be re-issued due to the addition of a test, or the correction of an error. When the report is re-issued, a notation of "REVISED REPORT" is to be placed on the page of the report along with a brief explanation of the correction and authorization initials and date. If it is not practical to include this information directly on the corrected page, a "text" flag can be placed in the result column of the report and a case narrative containing the explanation can be included with the report.

Additionally, a SAR report is required whenever data is changed after authorization. This allows assessment of why the data review process failed to detect an error prior to authorization and release of data and assures that corrective actions are implemented, when possible to prevent future occurrence.

12.4 Data Storage

All data is maintained in such a manner that the records are easily retrievable by authorized personnel. These records may be in electronic or hard copy form. Records may be retained either as original records or as true copies such as photocopies, microfilm, microfiche, or other accurate reproductions of the original records. Adequate information should be available to allow reconstruction of the final results.

12.4.1 Hard copy records storage

After the samples are completed, the hard copy raw and supporting data are stored and filed numerically, alphabetically, or chronologically by date or batch as appropriate for the type of record. The data are maintained in a secured area in the analytical unit in which the data were generated for approximately 1 year. Hard copies of the final reports with associated fieldsheets, COC forms and anomaly reports are filed chronologically in the front office of the Central Laboratory where they are maintained for approximately 3 years. Hard copy records are then transferred to storage boxes that are labeled with the month(s) and year(s) in which the records were generated and a brief content description. Each box is given a unique number and assigned an archive code. This code is entered into an archive log that includes a full description of the contents of each box. The archived boxes are stored on-site for approximately 5 years. Data which is expected to become part of a legal action will probably need to be maintained for a longer period of time. Legal counsel should be consulted in these cases. Data storage areas are protected against fire, theft, environmental deterioration and vermin. Data storage areas are regularly inspected as part of the Internal Audit program.

Sample data relating to known litigation samples and subsamples will be stored in a locked file cabinet or other designated secure area maintained by the Section Chief. An archive access log is maintained to document entry into this cabinet.

After the in-house storage period is up, records are processed and transferred to the State Records Center (SRC), 109 East Jones Street, Raleigh, NC. In accordance with the North Carolina Administrative Code, entry and access to the SRC building is limited to persons on official business. Access to stored records is restricted to the creating agency's staff. Persons other than an agency's staff must contact the appropriate agency and receive written permission prior to using records in the SRC. Procedures and forms required by the Center are identified in the State Records Center Handbook.

Currently, paper records are stored in their original form for a total of 10 years. After 10 years, the records are destroyed. Alternatively, some records may be processed for microfilming.

These records include:

- Correspondence between laboratory and client;
- All fieldsheets and documentation on the sampling event;
- All field and laboratory analytical records including supporting calibration, raw data, data reduction calculations, quality control information and all data output records (chromatograms, strip charts and other instrument response readout records); Original raw analytical data. This also includes, but it not limited to logbooks, QC samples and analytical samples, MDLs, control limits, standard preparation, method reference and data review records.

- All field and laboratory custody records including shipping receipts, sample transmittal forms, and sample disposal records;
- All notebooks, data forms, and logs pertaining to laboratory operations including sample receipt and log in;
- All records and reports of maintenance, calibration and inspection of equipment and instrumentation;
- All records concerning receipt, preparation and use of calibration standards;
- All statistical calculations used in data reduction and in determination of quality control limits;
- Quality Assurance records including, but not limited to, archived responses, PT sample results and raw data, internal and external audit findings and employee training records.
- Copies of final reports.

Retrieval of archived records (electronic or on paper) is done by referring to the archived records which contain the requester's name, agency, phone number, address, the archive code numbers, date, and the contents. Access to archived information is documented and requesters must complete a Records Retrieval form.

Earlier revisions of SOPs and the Quality Assurance Manual are also archived. The document's "date" indicates the time the policy or procedure was first adopted. Subsequent revision dates indicate when the next revision was adopted.

12.4.2 Electronic records storage

All in-lab data generated by computer systems are printed and archived as hard copies. When the capability exists, data is stored to tape, CD or on hard disc. The tapes, CDs or discs are labeled and stored at the individual workstations and serve as backup copies of the lab's raw data files. Currently, only GC/MS data for organics is backed up and electronically stored on a regular basis (weekly) to CDs. Chromatograms and data files are given a unique alphanumeric identification by the chemists initiating the analyses in each unit. These file identification numbers reflect either the date the sequence was initiated, the order in which the samples were analyzed or the sample identification and log numbers given by the client and listed in the DWR-WSS Laboratory LABWORKS™ LIMS.

Computer programs are verified initially and periodically by manual calculations and the calculations shall be kept on file.

All records must be protected from environmental degradation; stored under secure conditions to discourage tampering or vandalism; and must be cross-indexed by laboratory ID number or some other common identifier for easy retrieval.

DWR-Water Sciences Section LABWORKS™ LIMS data resides on a server maintained at the Western Data Center in Forest City NC. The server is programmed to backup daily. These daily tapes are retained for two weeks. Full back ups are done weekly and retained for one month.

Records, which are stored only on electronic media, must be maintained and supported in the laboratory by all hardware and software necessary for immediate data retrieval and review. If the laboratory changes its computer hardware or software, it will make provisions for transferring old data to the new system so that it remains retrievable.

12.4.3 Analytical notebooks/logbooks

Laboratory notebooks used to document pertinent information are stored within each analytical unit. Information contained in notebooks may include sample processing steps such as extractions and digestion records, instrument maintenance and routine checks, and standard and reagent preparations. Each notebook will have:

- Notebook Number/Identifier - Each notebook is issued a unique number that is determined sequentially or Identifier.
- Used for - Purpose and department of notebook.

- Date placed into use - This is the date that the notebook begins with entries.

Guidelines for Logbook use are as follows:

- Use permanent dark ink. No pencil entries are to be made.
- Corrections - Use a single line to cross out documentation errors leaving the original record visible. Date and initial the correction.
- Blank pages or space between the last entry and the bottom of the page must be "Z'd" through, initialed and dated.
- Data must be entered directly and consecutively into the notebook. It is not to be placed onto scratch paper and entered later.
- Entries added to previously signed pages must be dated, initialed and witnessed (if appropriate) below the new material.
- Sign and date each page upon completion.
- When pages are added to the notebook, they must be signed and dated across both the added page and the notebook page.

All notebooks are archived when they are complete and no longer in use.

In the organic areas, the following information is verified when applicable to the method being reviewed.

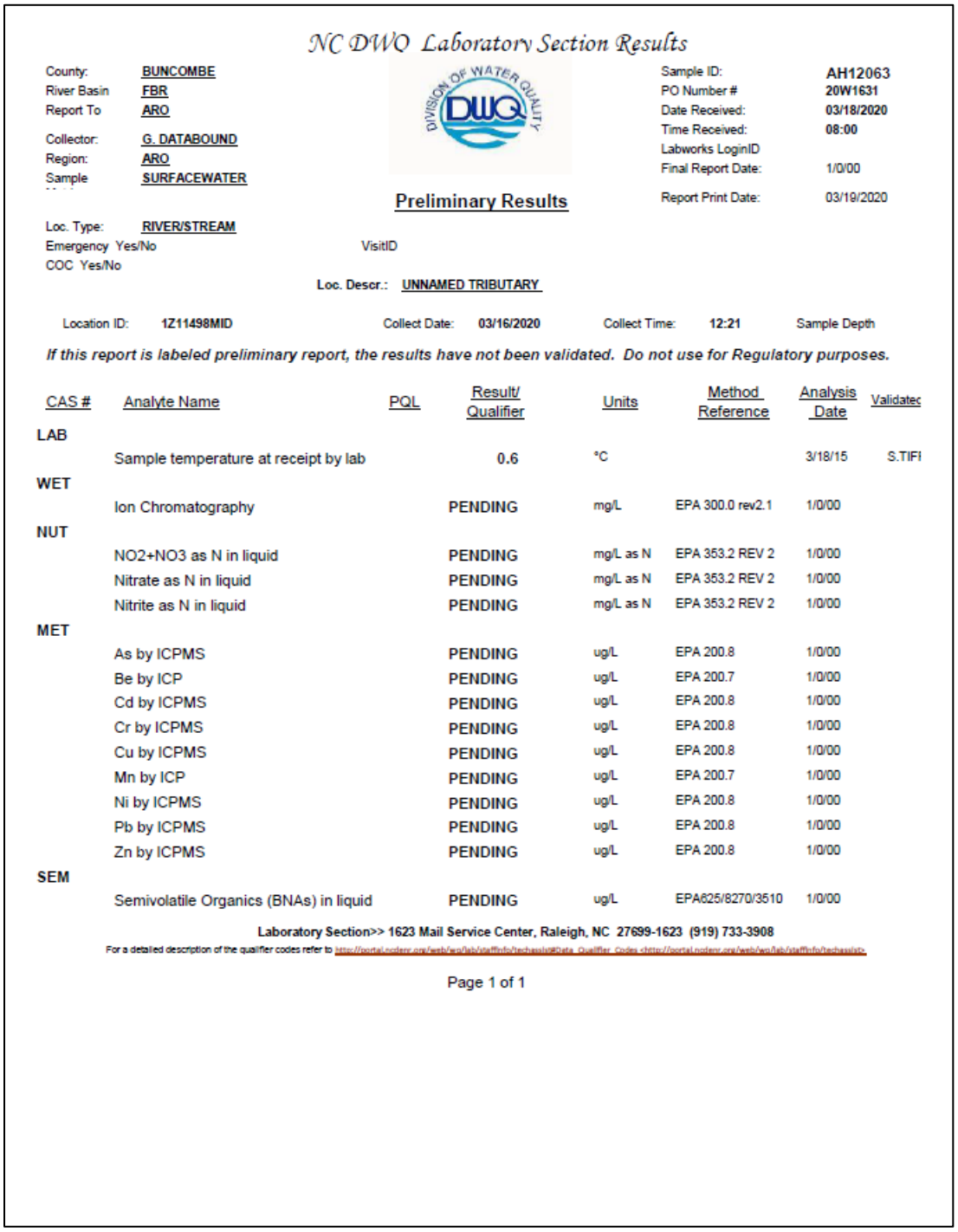
- Dates (e.g., extraction, calibration, analysis) and verify that holding times are met.
- Criteria for calibration, instrument tuning, internal standard areas, retention times, surrogate recoveries and analytical quality control results are checked.
- Method quality control data (e.g., blanks, spikes, duplicates, etc.) to assure the correct type and amount of checks are performed and results are within control limits.
- Compounds identified on the quantitation report were confirmed and agree with results reported on data sheets.
- Calculations such as total volatile hydrocarbons, soil concentrations, percent recoveries and dilutions are checked.
- Documentation of irregularities and if necessary data flagged when pre-established control limits are not met.

In the inorganic and microbiological analytical areas, the second analysts check the following items prior to results being entered into the data management system.

- Dates (extraction, digestion, calibration, incubation, analysis) and verify that holding times are met.
- Calibration criteria are met.

- Method quality control data (e.g., blanks, QCS, spikes, etc.) to assure the correct type and amount of checks are performed and results are within control limits.
- Data entry into calculation programs designed to calculate final results. Calculated results
- are checked against data bench worksheets for transcription errors.
- Documentation of any irregularity is documented and; if necessary, data flagged when pre-established control limits are not met.
- Reasonableness of data relationships (e.g., ammonia nitrogen results should not exceed total Kjeldahl nitrogen results).

Figure 12.1. Example report.



NC DWQ Laboratory Section Results

County: BUNCOMBE
River Basin FBR
Report To ARO
Collector: G. DATABOUND
Region: ARO
Sample SURFACEWATER

Sample ID: AH12063
PO Number # 20W1631
Date Received: 03/18/2020
Time Received: 08:00
Labworks LoginID
Final Report Date: 1/0/00
Report Print Date: 03/19/2020

Preliminary Results

Loc. Type: RIVER/STREAM
Emergency Yes/No
COC Yes/No
VisitID

Loc. Descr.: UNNAMED TRIBUTARY

Location ID: 1Z11498MID Collect Date: 03/16/2020 Collect Time: 12:21 Sample Depth

If this report is labeled preliminary report, the results have not been validated. Do not use for Regulatory purposes.

CAS #	Analyte Name	PQL	Result/ Qualifier	Units	Method Reference	Analysis Date	Validatec
LAB							
	Sample temperature at receipt by lab		0.6	°C		3/18/15	S.TIFI
WET							
	Ion Chromatography		PENDING	mg/L	EPA 300.0 rev2.1	1/0/00	
NUT							
	NO2+NO3 as N in liquid		PENDING	mg/L as N	EPA 353.2 REV 2	1/0/00	
	Nitrate as N in liquid		PENDING	mg/L as N	EPA 353.2 REV 2	1/0/00	
	Nitrite as N in liquid		PENDING	mg/L as N	EPA 353.2 REV 2	1/0/00	
MET							
	As by ICPMS		PENDING	ug/L	EPA 200.8	1/0/00	
	Be by ICP		PENDING	ug/L	EPA 200.7	1/0/00	
	Cd by ICPMS		PENDING	ug/L	EPA 200.8	1/0/00	
	Cr by ICPMS		PENDING	ug/L	EPA 200.8	1/0/00	
	Cu by ICPMS		PENDING	ug/L	EPA 200.8	1/0/00	
	Mn by ICP		PENDING	ug/L	EPA 200.7	1/0/00	
	Ni by ICPMS		PENDING	ug/L	EPA 200.8	1/0/00	
	Pb by ICPMS		PENDING	ug/L	EPA 200.8	1/0/00	
	Zn by ICPMS		PENDING	ug/L	EPA 200.8	1/0/00	
SEM							
	Semivolatile Organics (BNAs) in liquid		PENDING	ug/L	EPA625/8270/3510	1/0/00	

Laboratory Section>> 1623 Mail Service Center, Raleigh, NC 27699-1623 (919) 733-3908

For a detailed description of the qualifier codes refer to http://portal.ncdenr.org/web/wq/lab/staffinfo/techassist#Data_Qualifier_Codes <http://portal.ncdenr.org/web/wq/lab/staffinfo/techassist>

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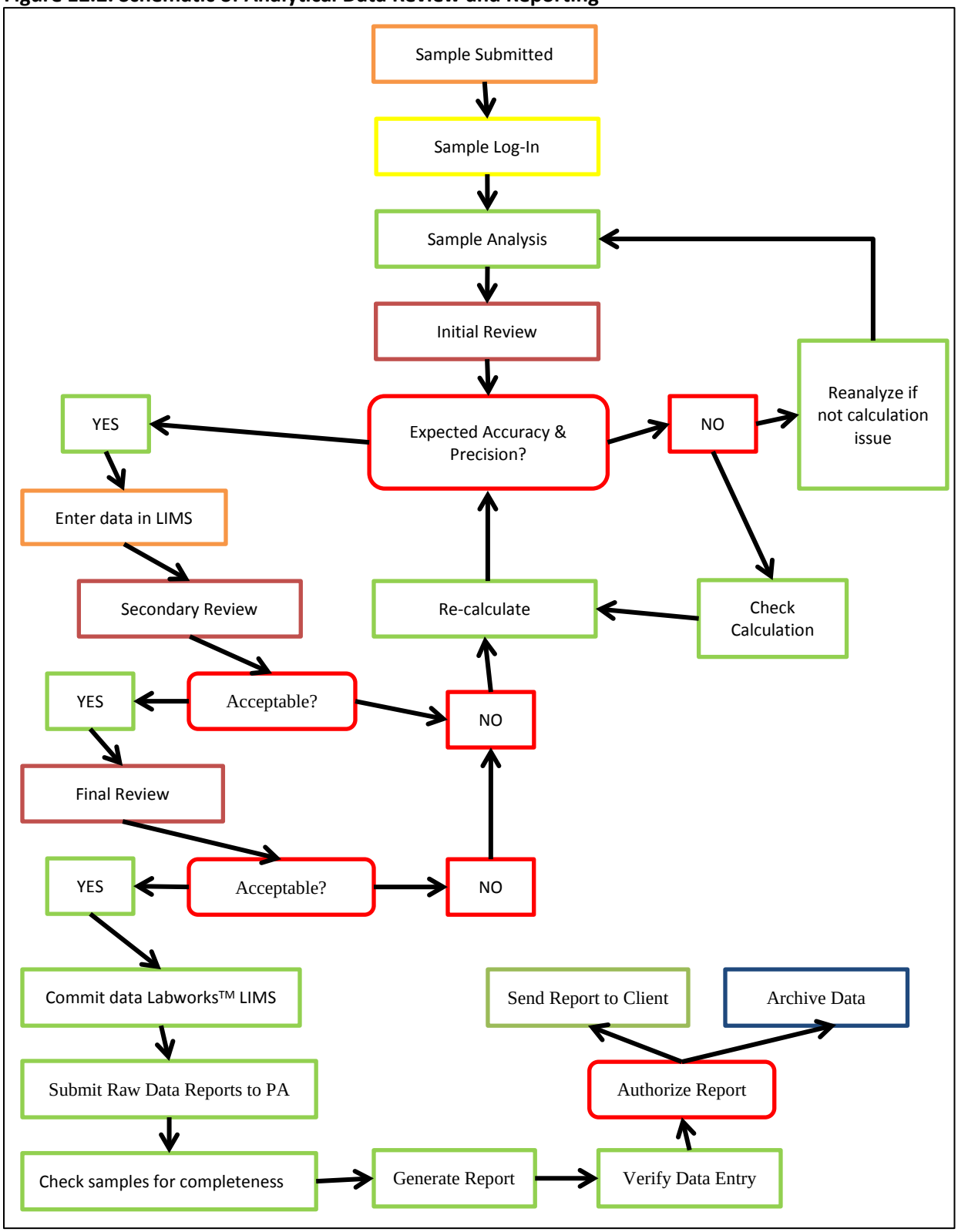
Figure 12.2. Schematic of Analytical Data Review and Reporting



13.0 Corrective Actions

Quality control elements are used to monitor and assess the validity of sampling and analysis activities. Formal corrective actions will be initiated if data are determined to be of questionable validity or if QC elements are not within required limits. When QC deficiencies or nonconformance situations exist, corrective action procedures provide a systematic approach to assess and restore laboratory analytical system integrity. For routine problems, the analyst corrects the problem and documents the process on the raw data, in the analytical run log or on the bench worksheet and a formal corrective action report is not required. Any laboratory employee that becomes aware of a problem related to one or more samples which cannot be immediately resolved, is responsible for initiating a corrective action investigation.

Quality control elements generally monitored by the DWR Water Sciences Section Chemistry Laboratory are listed in Section 5 (QA Targets for Precision, Accuracy and MDLs/PQLs), Section 9 (Calibration Procedures and Frequency) and Section 11 (Quality Control Checks and Routines to Assess Precision and Accuracy and Calculation of Method Detection Limits). Other method-specific QC elements are also monitored during routine operations. Table 13.1 identifies the QC elements routinely monitored by the Water Sciences Section Chemistry Laboratory, and lists the most appropriate corrective actions that should be taken if criteria are not met. Analytical SOPs detail algorithms for parameter-specific corrective action procedures.

Corrective actions are initiated based on either the internal QC checks, data validation or performance audits. Outside sources such as performance evaluation studies, split samples, as well as recommendations by EPA, will also initiate corrective actions.

13.1 Procedures for Reporting Exceptions

Significant deviations from standard policies or practices of the laboratory are reported to the client and documented with the analytical reports. Any samples that are prepared or analyzed beyond accepted holding times have a qualifier code reported with the data alerting the client to the fact that tests were conducted after the sample had expired. Similarly, the failure of any quality control checks is commented with the data via qualifier codes, directing the client to the Sample Anomaly Report or Sample Comments for details of failures. All other significant observations that do not conform to accepted practices or policies are documented and reported along with analytical results.

13.1.1 Sample Anomaly Report (SAR) Form

A Sample Anomaly Report documents laboratory quality control and quality assurance issues that warrant further investigation and associated correction actions (Figure 13.1).

Corrective action at the bench level is documented on the raw data or through the use of a SAR form which is generated in LABWORKS™ via the sample comments area of a sample report. The action is approved by the Peer Reviewer, Supervisor, and QA Officer and a copy is original is given to QA officer with the exception of the Organics Unit. The Organics Unit does not submit a paper SAR form to the QA officer; however, Samples Comments are reviewed by the Peer Reviewer, Supervisor and the QA Officer in LABWORKS™ .

13.1.2 Sample Condition Upon Receipt (SCUR) Form

The Sample Condition Upon Receipt (SCUR) form (Figure 13.2) is used by sample receipt personnel to document a nonconformance found during log-in. These are emailed to parties associated with sample. The original is retained in the sample report files. Section 7.0 describes how this form is used.

If there is a critical problem that requires immediate action in consultation with the client (e.g., samples received after holding time expired, insufficient sample volume), the client if notified immediately and the corrective action designed in consultation with the client is documented on the form.

13.1.3 Audit Reports and PT Results Reports

An additional type of corrective action documentation is a formally presented report of findings and resolutions for internal and external audits and PT results. These reports are filed in the QA Office with the audit and are distributed to parties interested in the audit findings.

13.2 Quality Control Batch Problems

A measurement system may be out of control when QC samples fall outside of the limits described in Section 5 (QA Targets for Precision, Accuracy and MDLs/PQLs), Section 9 (Calibration Procedures and Frequency) and Section 11 (Quality Control Checks and Routines to Assess Precision and Accuracy and Calculation of Method Detection Limits).

An entire batch of samples may require corrective action if these quality control criteria are not met. Supervisors or the analyst decide if re-analysis, re-extraction, etc. is necessary. Re-analysis would be noted in the folder with both sets of results included and clearly identified. The supervisor reviews both sets of data to determine if the problem has been resolved.

The EPA recommends the following guidelines for assessing acceptable data. If any data is determined to be out of control, one or all of these steps should be followed:

- Review the method with the analyst.
- Re-analyze the sample batch and evaluate the new results.
- Recalibrate the instrument with freshly prepared reagents and reanalyze the samples.
- Re-extract the samples per method.
- Evaluate the data and sample behavior and investigate any possible chemical interferences.
- Check instrument for possible maintenance requirements.
- Seek additional help from other analysts or provide additional training for laboratory personnel.
- Perform a system audit to evaluate corrective action measurements.

13.3 Sample Collection Problems

Samples may have to be re-collected if review of the data related to the sample collection, preservation, storage and custody indicate that representative, compliant samples were not obtained. The findings and corrective action procedures are documented on the appropriate SCUR or SAR form or in Labworks™.

13.4 Systematic Problems

Those problems of a procedural/system nature generally require the supervisor's or program manager's involvement. Examples might include previously reported data that has been affected by a situation requiring correction or if corrective action will impact project schedule or budget. The laboratory management staff is responsible for determining the significance of the problem and notifying the customer, of any event that casts significant doubt on the validity of the data if previous data is affected. This notification must be documented.

13.5 Departures from Documented Policies or Procedures

Due to the frequently unique nature of environmental samples, sometimes departures may be needed from documented policies and procedures. When the analyst encounters such a situation, the problem is presented to his/her supervisor for advice. The supervisor may elect to discuss it with the program manager or QA/QC Coordinator or may contact the client to decide on a logical course of action. Once an approach is agreed upon, the analyst notes it on the raw data or on a SAR forms. This information can then be supplied to the client in the form of a footnote or on the SAR.

13.6 External Corrective Actions

Any actions deemed necessary by external regulatory or certifying agencies such as EPA would be taken. These actions are most likely to arise from a system or performance audit, or from data review conducted by the agency.

13.7 Complaint Handling

Addressing complaints is a normal function of conducting business and a valuable tool for improving service to and relationships with clients.

The Water Sciences Section Laboratory is committed to resolving complaints and implementing suggestions for improvement expeditiously. All informal complaints, suggestions or requests for information are directed to the appropriate staff for resolution. The matter is passed through the chain of command, and ultimately, to the Section Chief who may investigate and direct the resolution if immediate resolution cannot be attained. Formal written complaints submitted to the Section are responded to in writing after investigation and resolution. Copies of responses are kept for reference.

13.8 Immediate vs. Long Term Corrective Action

Immediate corrective actions are necessary to correct or repair non-conforming equipment and systems. The analyst will most frequently be the one to identify the need for this action as a result of calibration checks and QC sample analysis.

Long-term corrective actions are necessary to eliminate causes of nonconformance. The need for such actions will probably be identified by audits. Examples of this type of action include:

- Staff training in technical skills or in implementing the quality assurance program.
- Rescheduling of laboratory routine to ensure analyses are performed within hold times.
- Identifying vendors to supply reagents of sufficient purity.
- Revision of quality assurance system or replacement of personnel.

Corrective action may also be initiated by various auditing authorities when deemed necessary. For either immediate or long-term corrective actions, steps comprising a closed-loop corrective action system are as follows:

- Define the problem.
- Assign the responsibility for investigating the problem.
- Investigate and determine the cause of the problem.
- Determine a corrective action plan to eliminate the problem.
- Assign and accept responsibility for implementing the corrective action.
- Establish effectiveness of the corrective action and implement the correction.
- Verify that the corrective action has eliminated the problem.

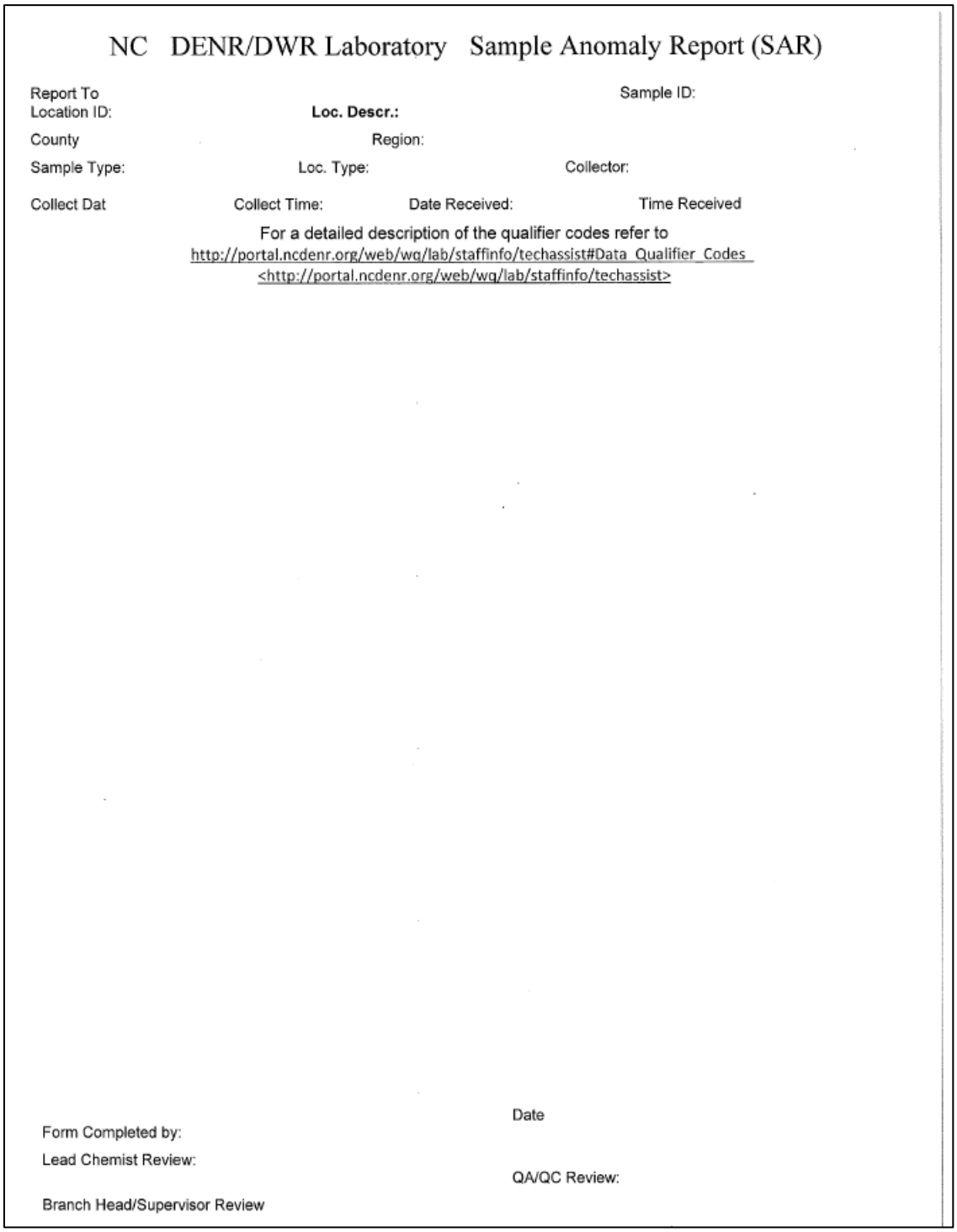
Table 13.1. Guide to Corrective actions for QC elements monitored by the Water Sciences Section.

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial Calibration	See method or Section 9	♦ Reanalyze standards. ♦ Review standard preparation logs for calculation/dilution errors or expired sources. ♦ Prepare fresh calibration standards and analyze new calibration curve. ♦ Evaluate instrument operation and perform preventive maintenance if needed.
Initial Calibration Verification Standard	See method or Section 9	♦ Reanalyze standard. ♦ Take corrective action for initial calibration.
Continuing Calibration Verification Standard	See method or Section 9	♦ Reanalyze standard. ♦ Review standard preparation logs for calculation/dilution errors or expired sources. ♦ Prepare fresh calibration standard and analyze. ♦ Take similar corrective action as for initial calibration.
Interference Check Standard (ICP only)	See method	♦ Reanalyze standard. ♦ Review standard preparation logs for calculation/dilution errors or expired sources. ♦ Prepare fresh standard and analyze. ♦ Evaluate instrument operation and perform preventive maintenance if needed.
MS tuning standard (GC/MS only)	See method	♦ Re-tune instrument using FC-43 (PFTBA). ♦ Reanalyze tune calibration standard (BFB/DFTPP). ♦ Review standard preparation logs for calculation/dilution errors or expired sources. ♦ Evaluate instrument operation and perform preventive maintenance if needed.
Method Blanks	Less than ½ the PQL with exceptions noted in analytical SOPs.	♦ Reanalyze the method blank. ♦ Determine the source of contamination (reagents, storage and analysis environment, equipment, improper cleaning of labware, reagent water, etc.). ♦ Re-prepare/re-analyze all associated samples. Note: Re-analysis may not be necessary if no samples in the batch contain the analyte(s) of interest detected in the method blank.
Matrix Spikes	See Section 5 or method	♦ Reanalyze. ♦ Review results for calculation errors. ♦ Review other QC samples in the analysis batch. Perform corrective actions for these QC samples. ♦ Analyze a LCS prepared in the same analytical batch as the suspect matrix spike. If the LCS meets criteria, report exception as due to possible matrix effect. ♦ If the LCS fails criteria, review standard preparation logs for calculation/dilution errors or expired solutions. ♦ Analyze the matrix spiking solution to confirm that is was prepared correctly. ♦ Re-prepare/re-analyze all associated samples.
Duplicates/ Matrix spike duplicates	See Section 5 or method	♦ Reanalyze. ♦ Review results for calculation errors. ♦ Review other QC samples in the analysis batch. Perform corrective actions for these QC samples. ♦ Analyze a LCS prepared in the same analytical batch. If the LCS meets criteria, report exception as due to possible matrix effect. ♦ Review sample preparation protocols to ensure that samples are homogenized before preparation/analysis. ♦ Re-prepare/re-analyze all associated samples.

Table 13.1. Guide to Corrective actions for QC elements monitored by the Water Sciences Section.

QC Activity	Acceptance Criteria	Recommended Corrective Action
Laboratory Control Sample	See Section 5	♦ Reanalyze. ♦ Review results for calculation errors. ♦ Review standard preparation logs for calculation/dilution errors or expired solutions. ♦ Review other QC samples in the analysis batch. If other QC samples in batch meet criteria, re-evaluate the need for corrective action. ♦ If the failed LCS is combined with failed matrix spikes or duplicates for the same spiked parameters, re-prepare/re-analyze all associated samples.
Surrogates	See method or analytical SOP	♦ Reanalyze. ♦ Evaluate the analytical results for unusual matrix effects (presence of chromatographic humps, etc.). ♦ Review results for calculation errors. ♦ Review standard preparation logs for calculation/dilution errors or expired solutions. ♦ Re-prepare/re-analyze. ♦ Review QC samples in the analysis batch. If other QC samples in batch meet criteria, additional corrective action may not be necessary.
Internal Standards	See method	♦ Follow method guidelines.
Trip blanks (VOA only)	Less than PQL	♦ Check related method blank for contamination.
Titrating Solutions	See method or analytical SOP	♦ Review results for calculation errors. ♦ Review standard preparation logs for calculation/dilution errors or expired solutions. ♦ Reanalyze all samples from last acceptable titration solution check.
Microbiology + and - controls for media	Should be + and -, respectively	♦ Reject medium.
Sample results	Calibration	♦ If the calibration fails for a target and the corresponding target is not detected, the results may be reported as <PQL or Nondetect if the PQL standard is analyzed and detected.
	Spike criteria limits	♦ If a limited list MS or LCS is high biased and no targets are detected above the PQL, results may be reported as <PQL/Nondetect. When a full compound spike is utilized, and the MS or LCS result is high biased, and the corresponding target is not detected, the result for the corresponding target may be reported as <PQL/Nondetect, regardless of the other targets.
	Surrogate criteria limits	♦ If surrogate recovery is high biased and no target is detected, the results are reported as <PQL/Nondetect.

Figure 13.1. Sample Anomaly Report (SAR) Form



NC DENR/DWR Laboratory Sample Anomaly Report (SAR)

Report To
Location ID: **Loc. Descr.:** Sample ID:

County Region:

Sample Type: Loc. Type: Collector:

Collect Dat Collect Time: Date Received: Time Received

For a detailed description of the qualifier codes refer to
http://portal.ncdenr.org/web/wq/lab/staffinfo/techassist#Data_Qualifier_Codes
<http://portal.ncdenr.org/web/wq/lab/staffinfo/techassist>

Date

Form Completed by:

Lead Chemist Review:

QA/QC Review:

Branch Head/Supervisor Review

Figure 13.2. Sample Condition Upon Receipt (SCUR) Report (Example)

NC DENR/DWR Chemistry Laboratory

Sample Condition Upon Receipt Anomaly Report (SCUR)

Lab Number: _____

Location Code: _____

Station Location: _____

Region: _____

County: _____

Collector: _____

Date Collected: _____

Date Received: _____

Priority: _____

Sample Type: _____

Affected Parameters: _____

The condition of these samples were not acceptable because:

Comments:

Corrective Action:
.

Cc:
FILE:
DB:
QA/QC:
LEAD CHEMIST:
BRANCH HEAD:

14.0 Performance and Systems Audits

Internal and external audits are conducted regularly at the DWR WSS Laboratory to ensure that the guidance provided in this document and in other related documents is followed. Internal audits are performed by the QA/QC coordinator, which is responsible for all QA/QC function in the laboratory, and members of the professional laboratory staff that do not normally work in the section or analytical unit being audited. External audits are conducted by persons who are not direct employees of the DWR WSS Laboratory (generally EPA Region 4) to provide an independent and unbiased review of laboratory operations.

NC DWR WSS Laboratory Certification Staff at least once every three years, performs a full scale audit/review of the DWR WSS Central and Asheville Regional Office Laboratories.

There are two types of audits: systems audits and performance audits

1) Systems audits include management system review, quality systems review and technical systems reviews. System audits involve an in-depth review and evaluation of some or all components of the analytical laboratory to determine the proper application of guidelines listed in the Quality Management Plan (QMP) and Quality Assurance Manual (QAM).

2) Performance audits are part of Quality Systems review and require the analysis of blind samples or other samples whose values are not known o the analytical areas. The DWR WSS Laboratory participates in Round Robin Studies for those parameters that do not have availability of purchasing blind samples. These results are used to evaluate the accuracy of the laboratory analytical system. Quality control elements are used to monitor and assess the validity of sampling and analysis activities. Formal corrective actions will be initiated if data are determined to be of questionable validity or if QC elements are not within required limits. When QC deficiencies or nonconformance situations exist, corrective action procedures provide a systematic approach to assess and restore laboratory analytical system integrity. For routine problems, the analyst corrects the problem and documents the process on the raw data, in the analytical run log or on the bench worksheet and a formal corrective action report is not required. Any laboratory employee that becomes aware of a problem related to one or more samples which cannot be immediately resolved, is responsible for initiating a corrective action investigation.

14.1 System Audits

Systems audits may be initiated either internally or externally.

14.1.1 Internal audits

It is the responsibility of the QA/QC Coordinator to plan and organize audits as required by a predetermined schedule and as requested by management. Such audits shall be carried out by the QA/QC Coordinator or trained and qualified personnel who are wherever resources permit, independent of the activity being audited. Personnel shall not audit their own activities except when it can be demonstrated that an effective audit will be carried out. System audits evaluate procedures and documentation in the laboratory. Additional audits may be necessary throughout the year to address specific project requirement, problem troubleshooting or issues that arise from other audits.

The QA/QC Coordinator conducts several systems audit during each calendar year which may be in combination with in house training. During these audits, one or more components of the laboratory will be reviewed to determine if that part is functioning in compliance with the Water Sciences Section Chemistry Laboratory Quality Management Plan, the Water Sciences Section Chemistry Laboratory Quality Assurance Manual, the approved standard operating procedures and approved methodology.

An audit report will include a list of deficiencies that must be addressed in order to correct or improve the laboratory operations.

(1) Selected systems will be audited every three months with a goal of auditing all systems once per year.

(2) The QA/QC Coordinator or WSS Laboratory Certification Staff will conduct the audits.

(3) The audit will consist of the submittal of blind samples or the random selection of previously reported samples, tracking of these samples through the system, evaluation of sample results, and a follow-up laboratory audit.

(4) System components to be audited will include, but are not limited to:

(j) All documentation associated with sample and data handling, to include linkage mechanism employed between all records for tracking documentation for any sample data result.

(ii) Use of established, approved procedures as outlined in this Quality Assurance Manual.

(iii) Personnel training records.

(iv) Proper execution of established procedures.

(v) Anomaly reports and follow-up to corrective actions from previous audits, external audits, performance testing samples or blind samples.

(vi) Review of Initial Demonstration Of Capabilities and Method Detection Limit Studies

(vii) Sample and data handling activities include:

[a] All sample log-in, routing and disposal.

[b] Sample preparations

[c] Method calibrations

[d] Sample analyses

[e] Data reduction, validation and reporting

[f] Preventive maintenance and repair procedures

[g] Standard and reagent preparation, documentation and storage

[h] Sample and waste disposal

[i] Container and labware decontamination

[j] QC management practices and assessment of analytical precision, accuracy and sensitivity

(5) Deficiency lists and associated corrective action orders will be formally communicated to responsible staff.

14.1.2 External Audits

External audits are performed when certifying agencies or clients submit a sample for analysis or conduct on-site inspections. It is the Water Sciences Section Chemistry Laboratory's policy to cooperate fully with certifying agencies. It is also our policy to comply fully with system audits conducted by regulatory agencies and clients. Currently, these regulatory agencies and clients include:

(1) EPA, Region IV; for selected systems, on an 18-60 month basis, depending on budget constraints; and

(2) USGS; selected systems; per-project basis

14.2 Proficiency Testing and Round Robin Samples

The lab participates in an annual Proficiency Testing (PT) program and Round Robin studies. Double blind PTs are obtained from a proficiency testing sample provider recognized by The NELAC Institute (TNI) and approved by the North Carolina Wastewater/Groundwater Laboratory Certification (NC WW/GW LC) program. Currently, PT providers must be accredited by the American Association for Laboratory Accreditation (A2LA) and Assured Calibration and Laboratory Accreditation (ACLASS). Round Robin studies are initiated by North Carolina Wastewater/Groundwater Laboratory Certification (NC WW/GWLC) program for Chlorophyll-*a*.

Full volume PTs and Round Robin samples follow normal hold time procedures and storage requirements unless the vendor-supplied directions instruct otherwise. Login will obtain the documentation provided with the PTs and fieldsheets will be reviewed by the QA/QC Coordinator or other designated staff prior to delivery to the analytical work areas. However, for PTs, holding time begins when the vial is opened.

All PT and Round Robin samples are analyzed and the results reported in a manner consistent with the routine analysis and reporting requirements of compliance samples and any other samples routinely analyzed by the laboratories. PT samples are entered into the laboratory samples receipt log as samples and tracked through the laboratory as routine environmental samples. Their preparation is also documented.

The lab retains all records necessary to facilitate historical reconstruction of the analysis and reporting of analytical results for PT samples for a minimum of five years. These records include a copy of the reporting form used by the laboratory to report the analytical results to the PT provider. If the analytical results are entered or uploaded electronically to a provider website, the laboratory retains a copy of the on-line data entry summary or similar documentation from the PT provider website.

Vials will be prepared as required in the instruction set provided with the samples. After preparation to full volume, the sample may be spiked, digested, concentrated, etc., as would be done for any normal sample requiring similar analysis. PT samples will not undergo multiple preparations, multiple runs, multiple methods (unless being used to evaluate multiple methods), or multiple dilutions, unless this is what would be done to a normal client sample. No special reviews shall be performed by operation and QA, unless this is what would be done to a normal client sample. To the degree that special report forms or login procedures are required by the PT supplier, it is reasonable that the laboratory would apply special review procedures, as would be done for any client requesting unusual reporting or login processes. Special QC samples can be included in the analytical run if this is what would be done with normal client samples under similar circumstances. North Carolina Wastewater/Groundwater Laboratory Certification (NC WW/GW LC) program arranges sample collection and submission and provides Round Robin Study instructions.

It is however recognized that PT samples are often not representative of "real world" samples either in their form (e.g., vials) or content (e.g., multiple target analyte hits) and as such, present the laboratory with special challenges. It is the policy of DWR that PT samples be treated as typical samples in the normal production process whenever this is possible. Further, where PT samples present special or unique problems in the normal production process they need to be treated differently, as would any special or unique request submitted by any client.

Whenever a DWR-WSS Laboratory fails a PT or Round Robin sample the WSS Laboratory must take the steps below. When greater than or equal to 80% of analytes are acceptable, for multi-analyte parameters (e.g., organic analyses), but one or more individual analytes are graded unacceptable, acceptable performance has been demonstrated for the parameter method technology. The laboratory, must, however, analyze a remedial PT for the individual analytes that were graded unacceptable.

NC DWR WSS Laboratory Certification Staff at least once every three years, performs a full scale audit/review of the DWR WSS Central and Asheville Regional Office Laboratories.

- Take steps to identify the root cause of the failure
- Take corrective action
- Report the corrective action taken to the Unit Supervisor and Environmental Program Supervisor
- Complete a DWR WSS Laboratory Corrective Action Report (CAR) (Note: Appendix I Corrective Action Report)
- Submit the Corrective Action Report to the QA Officer after management approval.
- Participate in a second blind PT or Round Robin Study.

No further action is necessary if the remedial PT results and corrective action report are acceptable.

Failure of a second remedial PT or Round Robin results in all data analysis for failed parameters being qualified OR halting analysis for failed parameter. When a remedial PT or follow up Round Robin is graded unacceptable for an individual analyte (constituting a second unacceptable result) for multi-analyte parameters, the laboratory must quality data for those individual analytes as “estimated” (whether detected or not) until acceptable results are obtained on two consecutive remedial PTs.

Internal and external audits are conducted regularly at the DWR WSS Laboratory to ensure that the guidance provided in this document and in other related documents is followed. Internal audits are performed by the QA/QC coordinator, which is responsible for all QA/QC function in the laboratory, and members of the professional laboratory staff that do not normally work in the section or analytical unit being audited. External audits are conducted by persons who are not direct employees of the DWR WSS Laboratory (generally EPA Region 4) to provide an independent and unbiased review of laboratory operations.

14.3 Quality Systems Management Review

The QA/QC Coordinator conducts an annual review of its quality systems to ensure its continuing suitability and effectiveness in meeting client and regulatory requirements and to introduce any necessary changes or improvements. Program Supervisors may be included in this process.

This review uses information generated during the preceding year to assess the "big picture" by ensuring that routine quality actions taken and reviewed on a semiannual basis are not components of systematic concerns. The semiannual review (Section 15) should keep the quality systems current and effective; therefore, the annual review is a formal senior management process to review specific existing documentation.

Significant issues from the following documentation are summarized by the QA/QC Coordinator prior to the review meeting.

- Matters arising from the previous annual review.
- Prior Quality Assurance Reports.
- Review of report reissue request.
- Minutes form prior meetings.
- Internal and External audits.

Consider:

- Adequacy of staff, equipment and facility resources.
- Future plans for resources and testing capability and capacity.

14.4 Corrective Actions

All deficiencies found during audits are reported to the Section Chief. Audit information is also provided through a semi-annual report. The Section Chief and QA/QC Coordinator agree upon a time frame for correction. The lab's response and corrective action procedures are evaluated by the QA/QC Coordinator and when acceptable are attached to each audit and filed. If issues arise that may require method suspension or restriction, the procedures in Section 13 are followed.

External audits often require written reports that include proof of correction. The QA coordinates this written response. Written responses to PT's are required. The response must address the reason for any "unacceptable or "check for error" result. In some cases is may be necessary for blind QC samples to be submitted to the laboratory to show a return to control.

14.5 Report Audits

Routine report audits are the responsibility of the laboratory Quality Assurance Officer. The QA Officer performs an independent systems review of reports generated by the laboratory. The QA Officer will quarterly review random final reports for completeness (proper signature, login entry etc.). The QA Officer may review one or more parameters data of final report. Areas for review may include COC, correspondence with the analytical request, batch QC status, completeness of any corrective action statements, 5% of calculations, format, holding time, sensibility and completeness of the contents. A list of reports reviewed is maintained in an audit file.

15.0 Quality Assurance Reports

Quality assurance reports to laboratory management are required to keep them informed about how the laboratory QA program is progressing. Items in which performance is not satisfactory are addressed and a plan for corrective action prepared and implemented.

15.1 Internal Reports

A semi-annual QA report is prepared by the QA/QC Coordinator. This information is circulated to the Section Chief and branch managers. An example format with the minimum required topics for reporting is illustrated in Figure 15.1.

Reports of internal laboratory audits and all performance audits are addressed to the Section Chief, who in turn distributes them to the management staff for corrective action, as needed. Results of external laboratory audits are routed to the management staff through the Section Chief for corrective action, if required. The QA/QC Coordinator ensures that corrective actions are implemented.

15.2 External Reports

The QA/QC Coordinator will prepare external QA reports for specific projects, agencies or clients that may require it. These will be addressed to the client or data user at the frequency and in the format mandated by the specific project requirements.

Figure 15.1. Semi Annual QA Report to Management Format

QA SEMI ANNUAL REPORT TO MANAGEMENT

LABORATORY:
ANALYTICAL UNIT:
PERIOD COVERED:
PREPARED BY:

TO: Section Chief
CC: Environmental Program Supervisor(s)

KEY ISSUES:

1.
2.
3.

A. SOPs
- The following SOPS were finalized (include updated SOP summary with report):
- The following SOPs are in QA for review:
- The following SOPs are due to QA:

B. CORRECTIVE ACTION REPORTS (SARs/SCURs)

- Highlights:

C. MDLs and IDOCs
- MDLs completed:
- IDOCs completed:

D. AUDITS
- INTERNAL AUDITS (The following internal audits were performed - include method and general)
- EXTERNAL AUDITS (Include source, date, highlights, date corrective action package is due, progress on corrective actions)

E. PE SAMPLES
- The following PE samples are now in-house (due dates):
- The following PE results have been received (results presented as a percentage by Unit, discuss corrective action)

F. TRAINING
- Training record issues

G. MISCELLANEOUS

16.0 Selected References

"Definition and Procedure for the Determination of the Method Detection Limit- Revision 1.11", 40 CFR Part 136, Appendix B. July 1, 2011

Handbook for Analytical Quality Control in Water and Wastewater, EPA 600/4-79-019, March 1979.

Methods for Chemical Analysis of Water and Wastes, USEPA Office of Research and Development, Rev. 3/83. Cincinnati, OH, 3/83; EPA 600/4-79-020.

Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW-846; 3rd edition (9/86), with Final Updates I (7/92), II (9/94), IIA (9/93) and IIB (1/95); USEPA Office of Solid Waste and emergency Response, Washington, D.C.

Method for the Determination of Organic Compounds in Drinking Water, Supplement I, EPA 600/4-90/020, July 1990.

Standard Methods for the Examination of Water and Wastewater (designated SM), 18th Edition, American Public Health Association, Washington, DC, 1992.

Standard Methods for the Examination of Water and Wastewater (designated SM), 19th Edition, American Public Health Association, Washington, DC, 1995.

Standard Methods for the Examination of Water and Wastewater (designated SM), 20th Edition, American Public Health Association, Washington, DC, 1998.

Standard Methods for the Examination of Water and Wastewater (designated SM), 21st Edition, American Public Health Association, Washington, DC, 2005.

Standard Methods for the Examination of Water and Wastewater (designated SM), 22nd Edition, American Public Health Association, Washington, DC, 2012.

Code of Federal Regulations, Title 40, Part 136, U.S. Government printing office, Washington, D.C., July 1993.

Chemical Hygiene Plan, North Carolina Division of Water Resources, Water Sciences Section - Central Laboratory, 11/17/2014

Chemical Hygiene Plan, North Carolina Division of Water Resources, Water Sciences Section - Asheville Regional Office Laboratory,11.17.2014

USEPA. 1978. Microbiological Methods for Monitoring the Environment (Water and Wastes), Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, OH

40 CFR 136 2012 Method Update Rule (MUR), May 2012

17.0 Appendices

Appendix I. Corrective Action Report Form

Corrective Action Report Form

NC DWR WSS Chemistry Laboratory	Corrective Action Report (CAR)
Non-conformance type:	☐Sampling ☐Sample Receiving ☐Proficiency Testing ☐Calibration ☐Analysis ☐QC ☐External Audit ☐Other:
CAR Initiated by:	Date Initiated:

Date	Description of Non-conformance:
Date	**Description of Root Cause Analysis:**
Date	**Trouble shooting:**
Date	**Corrective Actions Taken to Prevent Recurrence:**
	Sample Data Requiring Qualification/Rejection:
Date	**Follow-up Investigation/Continuous Monitoring:**
	Corrective Action Successful: ☐Yes ☐No
	Supporting Documents Attached: ☐Yes ☐No
	Date CAR Closed: _____ Supervisor Signature/date:_____ QAO Signature/date:_____

Document PT analyst. PT analyst should perform remedial PT analysis.

Appendix II. NC DWR WSS Laboratory Qualifier Codes

Symbol	Definition
A	Value reported is the mean (average) of two or more determinations. This code is to be used if the results of two or more discrete and separate samples are averaged. These samples shall have been processed and analyzed independently (e.g. field duplicates, different dilutions of the same sample). This code is not required for BOD, coliform or acute/chronic metals reporting since averaging multiple results for these parameters is fundamental to those methods or manner of reporting. 1. The reported value is an average, where at least one result is qualified with a "U". The PQL is used for the qualified result(s) to calculate the average.
B	Results based upon colony counts outside the acceptable range and should be used with caution. This code applies to microbiological tests and specifically to **membrane filter (MF)** colony counts. It is to be used if less than 100% sample was analyzed and the colony count is generated from a plate in which the number of colonies exceeds the ideal ranges indicated by the method. These ideal ranges are defined in the method as: *Fecal coliform or Enterococcus bacteria: 20-60 colonies* *Total coliform bacteria: 20-80 colonies* 1. Countable membranes with less than 20 colonies. Reported value is estimated or is a total of the counts on all filters reported per 100 ml. 2. Counts from all filters were zero. The value reported is based on the number of colonies per 100 ml that would have been reported if there had been one colony on the filter representing the largest filtration volume (reported as a less than "<" value). 3. Countable membranes with more than 60 or 80 colonies. The value reported is calculated using the count from the smallest volume filtered and reported as a greater than ">" value. 4. Filters have counts of both >60 or 80 and <20. Reported value is estimated or is a total of the counts on all filters reported per 100 ml. 5. Too many colonies were present; too numerous to count (TNTC). TNTC is generally defined as >150 colonies. The numeric value represents the maximum number of counts typically accepted on a filter membrane (60 for fecal or enterococcus and 80 for total), multiplied by 100 and then divided by the smallest filtration volume analyzed. This number is reported as a greater than value. 6. Estimated Value. Blank contamination evident. 7. Many non-coliform or non-enterococcus colonies or interfering non-coliform or non-enterococcus growth present. In this competitive situation, the reported value may under-represent actual density. Note: A "B" value shall be accompanied by justification for its use denoted by the numbers listed above (e.g., B1, B2, etc.). Note: A "J2" should be used for spiking failures.
BB	This code applies to **most probable number (MPN)** microbiological tests. 1. No wells or tubes gave a positive reaction. Value based upon the appropriate MPN Index and reported as a less than "<" value. 2. All wells or tubes gave positive reactions. Value based upon the MPN Index and reported as a greater than ">" value. Note: A "BB" value shall be accompanied by justification for its use denoted by the numbers listed above (e.g., BB1, BB2, etc.).
C	Total residual chlorine was present in sample upon receipt in the laboratory; value is **estimated**. Generally applies to cyanide, phenol, NH3, TKN, coliform, and organics.
G	A single quality control failure occurred during biochemical oxygen demand (BOD) analysis. The sample results should be used with caution. 1. The dissolved oxygen (DO) depletion of the dilution water blank exceeded 0.2 mg/L. 2. The bacterial seed controls did not meet the requirement of a DO depletion of at least 2.0 mg/L and/or a DO residual of at least 1.0 mg/L. 3. No sample dilution met the requirement of a DO depletion of at least 2.0 mg/L and/or a DO residual of at least 1.0 mg/L. 4. Evidence of toxicity was present. This is generally characterized by a significant increase in the BOD value as the sample concentration decreases. The reported value is calculated from the highest dilution representing the maximum loading potential and should be considered an **estimated** value. 5. The glucose/ glutamic acid standard exceeded the range of 198 ± 30.5 mg/L. 6. The calculated seed correction exceeded the range of 0.6 to 1.0 mg/L. 7. Less than 1 mg/L DO remained for all dilutions set. The reported value is an **estimated** greater than value and is calculated for the dilution using the least amount of sample. 8. Oxygen usage is less than 2 mg/L for all dilutions set. The reported value is an **estimated** less than value and is calculated for the dilution using the most amount of sample. 9. The DO depletion of the dilution water blank produced a negative value. Note: A "G" value shall be accompanied by justification for its use denoted by the numbers listed above (e.g., G1, G2, etc.).
J	**Estimated** value; value may not be accurate. This code is to be used in the following instances: 1. Surrogate recovery limits have been exceeded. 2. The reported value failed to meet the established quality control criteria for either precision or accuracy. 3. The sample matrix interfered with the ability to make any accurate determination.

J	4. The data is questionable because of improper laboratory or field protocols (e.g., composite sample was collected instead of grab, plastic instead of glass container, etc.). 5. Temperature limits exceeded (samples frozen or >6°C) during transport or not verifiable (e.g., no temperature blank provided): non-reportable for NPDES compliance monitoring. 6. The laboratory analysis was from an unpreserved or improperly chemically preserved sample. The data may not be accurate. 7. This qualifier is used to identify analyte concentration exceeding the upper calibration range of the analytical instrument/method. The reported value should be considered estimated. 8. Temperature limits exceeded (samples frozen or >6°C) during storage, the data may not be accurate. 9. The reported value is determined by a **one-point estimation** rather than against a regression equation. The estimated concentration is less than the laboratory practical quantitation limit and greater than the laboratory method detection limit. 10. Unidentified peak; estimated value. 11. The reported value is determined by a **one-point estimation** rather than against a regression equation. The estimated concentration is less than the laboratory practical quantitation limit and greater than the instrument noise level. *This code is used when an MDL has not been established for the analyte in question.* 12. The calibration verification did not meet the calibration acceptance criterion for **field parameters**. Note: A "J" value shall be accompanied by justification for its use denoted by the numbers listed above (e.g., J1, J2, etc.). A "J" value shall not be used if another code applies (e.g., N, V, M).
M	Sample and duplicate results are "out of control". The sample is non-homogenous (e.g., VOA soil). The reported value is the lower value of duplicate analyses of a sample.
N	Presumptive evidence of presence of material; **estimated** value. This code is to be used if: 1. The component has been tentatively identified based on mass spectral library search. 2. There is an indication that the analyte is present, but quality control requirements for confirmation were not met (i.e., presence of analyte was not confirmed by alternate procedures). 3. This code shall be used if the level is too low to permit accurate quantification, but the **estimated** concentration is less than the laboratory practical quantitation limit and greater than the laboratory method detection limit. *This code is not routinely used for most analyses.* 4. This code shall be used if the level is too low to permit accurate quantification, but the **estimated** concentration is less than the laboratory practical quantitation limit and greater than the instrument noise level. *This code is used when an MDL has not been established for the analyte in question.* 5. The component has been tentatively identified based on a retention time standard.
Q	Holding time exceeded. These codes shall be used if the value is derived from a sample that was received, prepared and/or analyzed after the approved holding time restrictions for sample preparation and analysis. The value does not meet NPDES requirements. 1. Holding time exceeded prior to receipt by lab. 2. Holding time exceeded following receipt by lab.
P	Elevated PQL* due to matrix interference and/or sample dilution.
S	Not enough sample provided to prepare and/or analyze a method-required matrix spike (MS) and/or matrix spike duplicate (MSD).
U	Indicates that the analyte was analyzed for but not detected above the reported practical quantitation limit*. The number value reported with the "U" qualifier is equal to the laboratory's practical quantitation limit*.
X	Sample not analyzed for this constituent. This code is to be used if: 1. Sample not screened for this compound. 2. Sampled, but analysis lost or not performed-field error. 3. Sampled, but analysis lost or not performed-lab error. Note: an "X" value shall be accompanied by justification for its use by the numbers listed.
V	Indicates the analyte was detected in both the sample and the associated blank. Note: The value in the blank shall not be subtracted from the associated samples. 1.The analyte was detected in both the sample and the method blank. 2.The analyte was detected in both the sample and the field blank
	Elevated PQL* due to insufficient sample size.
Z	The sample analysis/results are not reported due to: 1. Inability to analyze the sample. 2. Questions concerning data reliability. The presence or absence of the analyte cannot be verified.

	Supporting Definitions listed below
MDL	A Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the true value is greater than zero and is determined in accordance with 40 CFR Part 136, Appendix B.
ML	Minimum Levels are used in some EPA methods. A Minimum Level (ML) is the lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method - specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the nearest factor of 10 multiple (i.e., 1, 2, or 5). For example, MDL = 1.4 mg/L; ML = 1.4 mg/L x 3.18 = 4.45 rounded to the nearest factor of 10 multiple (i.e., 5) = 5.0 mg/L
***PQL**	The Practical Quantitation Limit (PQL) is defined as the lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. PQLs are subjectively set at some multiple of typical MDLs for reagent water (generally 3 to 10 times the MDL depending upon the parameter or analyte and based on the analyst's best professional judgement, the quality and age of the instrument and the nature of the samples) rather than explicitly determined. PQLs may be nominally chosen within these guidelines to simplify data reporting and, where applicable, are generally equal to the concentration of the lowest non-zero standard in the calibration curve. PQLs are adjusted for sample size, dilution and % moisture. For parameters that are not amenable to MDL studies, the PQL may be defined by the sample volume and buret graduations for titrations or by minimum measurement values set by the method for method-defined parameters (e.g., BOD requires a minimum DO depletion of 2.0 mg/L, fecal coliform requires a minimum plate count of 20 cfu, total suspended residue requires a minimum weight gain of 2.5 mg, etc.). Additionally, some EPA methods prescribe Minimum Levels (MLs) and the lab may set the PQL equal to this method-stated ML. Determination of PQL is fully described in the laboratory's analytical Standard Operating Procedure (SOP) document.
06/25/2015	

Appendix III. CHP Orientation Training Form

CHP ORIENTATION TRAINING

Date of Training: _____

Name of Employee: _____

Trainers : _____
(and initials)

☐ **Hazard Communication Review** **(29 CFR 1910.1200)**
Hazard Classes of Chemicals used in the Laboratory
Safety Data Sheets
Labeling
Storage and Handling Chemicals

☐ **CHP Review** **(29 CFR 1910.1450)**
Emergency Actions and Notification
Fire Prevention Guidelines
Housekeeping Rules, Clothing and Personal Items

☐ **Personal Protective Equipment**

☐ **Evacuation Routes**

☐ **General Laboratory Hazards**
Recognizing work area hazards
Electrical Hazards
Compressed Gases
Vacuum
Radioactive Hazards
Noise Exposure
Fume Hood Use

☐ **Chemicals used in the Laboratory**
Extremely Hazardous and Toxic Materials
Transporting Chemicals
Chemical Waste Disposal
Biological Waste Disposal

Appendix IV. DWR WSS Laboratory Program Records Retention and Disposition Schedule

DEPARTMENT OF ENVIRONMENT AND NATURAL RESOURCES
ASSISTANT SECRETARY FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER QUALITY
LABORATORY SECTION

Program Records Retention and Disposition Schedule

The Program Records Retention and Disposition Schedule and retention periods governing the records series listed herein are hereby approved. In accordance with the provisions of Chapters 121 and 132 of the General Statutes of North Carolina, it is agreed that the records of the

LABORATORY SECTION

do not and will not have further official use or value for administrative, research, or reference purposes after the respective retention periods specified herein. The N.C. Department of Cultural Resources consents to the destruction or other disposition of these records in accordance with the retention and disposition instructions specified in this schedule. However, records subject to audit or those legally required for ongoing official proceedings must be retained until released from such audits or official proceedings, notwithstanding the instructions of this schedule. **Public records including electronic records not listed in this schedule or in the *General Schedule for State Agency Records* are not authorized to be destroyed.**

The

LABORATORY SECTION

agrees to destroy, transfer or dispose of records in the manner and at the times specified herein. This schedule is to remain in effect until superseded.

APPROVAL RECOMMENDED

Lloyd E. Inman, Jr., Chief Records Officer
Department of Environment and Natural Resources

Gregory J. Thorpe, Acting Director
Division of Water Quality

David J. Olson, Director
Division of Historical Resources

APPROVED

William G. Ross, Jr., Secretary
Department of Environment and Natural Resources

Lisbeth C. Evans, Secretary
Department of Cultural Resources

February 25, 2002

AWH

PROGRAM RECORDS RETENTION AND DISPOSITION SCHEDULE AMENDMENT

DEPARTMENT OF ENVIRONMENT AND NATURAL RESOURCES
ASSISTANT SECRETARY FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER QUALITY
LABORATORY SECTION

Amend the program records retention and disposition schedule approved February 25, 2002 by changing the description for Item 2615 as shown on substitute page dated April 18, 2006.

APPROVAL RECOMMENDED

Lloyd E. Inman, Jr., Chief Records Officer
Department of Environment and Natural Resources

Alan W. Klimek, Director
Division of Water Quality

David Brook, Director
Division of Historical Resources

APPROVED

William G. Ross, Jr., Secretary
Department of Environment and
Natural Resources

Lisbeth C. Evans, Secretary
Department of Cultural Resources

April 18, 2006

AWH

DEPARTMENT OF ENVIRONMENT AND NATURAL RESOURCES
ASSISTANT SECRETARY FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER QUALITY
LABORATORY SECTION

ITEM 2615. WATER QUALITY DATA FILE.
Records in paper and electronic formats concerning laboratory forms listing results of analyses of samples for the Water Quality program. File also includes laboratory worksheets listing laboratory numbers, sample sizes, determinations of analyses; listings of results of analyses; and other related records. Files dated after January 1, 1997 do not include Ambient Stream Monitoring and Sediment and Fish Tissue Laboratory Sheets. For this information, see Environmental Sciences Section, Ambient Stream Monitoring and Sediment and Fish Tissue Laboratory Sheets File (Item 17431). Amended 4-18-06

DISPOSITION INSTRUCTIONS: Destroy in office electronic records when reference value ends. Transfer paper records to the State Records Center after 5 years. Records will be held for agency in the State Records Center 5 additional years and then destroyed. Destroy records currently stored in the State Records Center 5 years from date received.

ITEM 2617. GROUNDWATER DATA FILE.
Records in paper and electronic formats concerning laboratory forms listing results of analyses of samples for the Groundwater program. File also includes laboratory worksheets listing laboratory numbers, sample sizes, determinations of analyses; listings of results of analyses; and other related records.

DISPOSITION INSTRUCTIONS: Destroy in office electronic records when reference value ends. Transfer paper records to the State Records Center after 5 years. Records will be held for agency in the State Records Center 5 additional years and then destroyed. Destroy records currently stored in the State Records Center 5 years from date received.

ITEM 2619. AIR QUALITY DATA FILE.
Records in paper and electronic formats concerning laboratory forms listing results of analyses of samples for the Air Quality program. File also includes laboratory worksheets listing laboratory numbers, sample sizes, determinations of analyses; listings of results of analyses; and other related records. Records no longer being created.

DISPOSITION INSTRUCTIONS: Destroy records currently held in the State Records Center 5 years from date received.

ITEM 3580. TECHNICAL SERVICES DATA FILE.
Records in paper and electronic formats concerning laboratory forms detailing the analysis of environmental samples for the Technical Services Program. File includes laboratory worksheets, log summary sheets, data reports, quality control data, chain of custody records, recorder charts, and other related data. Records are no longer being created.

DISPOSITION INSTRUCTIONS: Destroy in office electronic records when reference value ends. Transfer paper records to the State Records Center after 5 years. Records will be held for agency in the State Records Center 5 additional years and then destroyed. Destroy records currently stored in the State Records Center 5 years from date received.

ITEM 3964. ORGANIC ANALYSES DATA FILE.
Records in paper and electronic formats concerning laboratory forms listing results of organic analyses of samples for Air Quality, Water Quality, and Groundwater programs. File also includes laboratory worksheets listing laboratory numbers, sample sizes, determinations of analyses; listings of results of analyses; and other related records.

DISPOSITION INSTRUCTIONS: Destroy in office electronic records records when reference value ends. Transfer paper records to the State Records Center after 5 years. Records will be held for agency in the State Records Center 5 additional years and then destroyed. Destroy records currently stored in the State Records Center 5 years from date received.

DEPARTMENT OF ENVIRONMENT AND NATURAL RESOURCES
ASSISTANT SECRETARY FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER QUALITY
LABORATORY SECTION

ITEM 3965. METALS ANALYSES DATA FILE.
Records in paper and electronic formats concerning laboratory forms listing results of metals analyses of samples for Air Quality, Water Quality, and Groundwater programs. File also includes laboratory worksheets listing laboratory numbers, sample sizes, determinations of analyses; listings of results of analyses; and other related records.

DISPOSITION INSTRUCTIONS: Destroy in office electronic records records when reference value ends. Transfer paper records to the State Records Center after 5 years. Records will be held for agency in the State Records Center 5 additional years and then destroyed. Destroy records currently stored in the State Records Center 5 years from date received.

ITEM 3966. NUTRIENT ANALYSES DATA FILE.
Records in paper and electronic formats concerning forms listing results of nutrient analyses of samples for Air Quality, Water Quality, and Groundwater programs. File also includes laboratory worksheets listing laboratory numbers, sample sizes, determinations of analyses; listings of results of analyses; and other related records.

DISPOSITION INSTRUCTIONS: Destroy in office electronic records when reference value ends. Transfer paper records to the State Records Center after 5 years. Records will be held for agency in the State Records Center 5 additional years and then destroyed. Destroy records currently stored in the State Records Center 5 years from date received.

ITEM 17600. CHEMISTRY LABORATORIES CERTIFICATIONS FILE.
Records concerning laboratories certified by the Division of Water Quality to perform chemical processes of wastewater analysis. File includes applications for certification, correspondence, listings of fees collected, evaluations, and other related records.

DISPOSITION INSTRUCTIONS: Transfer to the State Records Center after 5 year(s). Records will be held for agency in the State Records Center 5 additional years and then destroyed.

ITEM 17602. LABORATORY ADMINISTRATIVE AND MANAGEMENT FILE.
Records concerning the operation and management of the Laboratory Section. File includes correspondence, reference copies of purchase orders and requisitions, printing and travel procedures, and other related records.

DISPOSITION INSTRUCTIONS: Destroy in office when reference value ends.

ITEM 17605. CHEMICAL SAFETY DATA SHEETS FILE.
Chemical safety data sheets listing chemicals used in the laboratory, procedures to follow if the chemical is spilled or ingested, and other related records. (File is maintained in accordance with 13 NCAC 7C.0101(a)(99), G.S. 95-191, and Title III of the Superfund Amendments and Reauthorization Act of 1986.)

DISPOSITION INSTRUCTIONS: Retain in office permanently.

Appendix V. NC DWR Water Sciences Section (WSS) Laboratory Prioritization Policy - 2015

Water Sciences Section (WSS) Laboratory Sample Prioritization Policy

This is a restatement of the WSS Laboratory policy regarding samples and their sample analysis priority.

Our goal at the WSS Laboratories is to analyze all samples as quickly as possible without jeopardizing data quality, and always within the published holding time. There are a number of factors which may affect routine turnaround times including, but not limited to, sample load, transport, preparation, extraction time, clean-up, troubleshooting/re-analysis, data evaluation and reporting. Routine samples are batched for cost and resource efficiency.

Occasionally, samples must be given higher priority and this document outlines the WSS laboratories policy on sample prioritization. Sample collectors are asked to first ask for approval from their supervisor to designate a sample as an "emergency", and second, to limit using the emergency designation to only those samples where immediate turnaround is required. Analysts are required to keep alert for emergency samples and where emergency samples are in the analytical and reporting process.

Note: The Chain of Custody (COC) designation does not impart any priority in terms of order or turnaround time of analyses; COC simply ensures the integrity of the sample through traceable documentation of possession and handling of the sample from time of collection through the process of sample submission and analysis and review.

Priority of samples for processing is listed below, the top being the highest priority.

- Office of the Secretary Priority Samples
- Emergency Samples
- Routine Samples

Samples designated as priority by the Office of the Secretary and Emergency samples preempt all other routine sample analyses even if it means those routine samples will not meet the required hold time. The immediate WSS laboratory unit supervisor is contacted whenever events beyond lab staff control occur and prevent Office of the Secretary Priority or Emergency samples preparation and or analysis within 24 hours of receipt. This alert to the unit supervisor prompts immediate communication between the supervisor and the collector.

Timely communication is important between analyst and supervisor as well as supervisor and collector for the following reasons:

a. Critical decisions may be hinging on those sample results. For example: A homeowner's water supply well has suspected volatile organics contamination and decisions must be made quickly regarding the necessity of a health risk assessment or whether it is safe to consume that water.
b. Timely communication may also enable the collector to resample, if necessary.

For routine samples, the laboratory unit supervisor is immediately alerted when an event occurs such as equipment failure, weather, additional runs are required, etc., which will prevent timely turnaround of sample results. The unit supervisor then makes contact with the sample collector.

In addition, samples will at times present very unusual results. While reviewing data if unusual results are found, the results and information are shared with the supervisor as soon as possible. Examples of unusual samples results are: high levels of Cyanide in a water sample, high level contamination in blanks, etc. Once again, the supervisor is notified immediately. When notified of unusual findings, supervisors can then communicate results and provide consultation to the collector.

Appendix VI. North Carolina (NC) Division of Water Resources (DWR) Water Sciences Section (WSS) Chemistry Laboratories Initial Demonstration of Capability (IDOC) Policy - May 09, 2016 **North Carolina (NC) Division of Water Resources (DWR) Water Sciences Section (WSS) Chemistry Laboratories Initial Demonstration of Capability (IDOC) Policy - May 09, 2016**

Initial Demonstration of Capability -The analysis of a set of known concentration samples or standards used to document an analyst's ability to perform an analytical procedure correctly. The results of the analyses must meet the precision and accuracy criteria of the method and in the absence of method criteria, meet the precision and accuracy of the laboratory criteria.

Analyst initial demonstration of capability shall be performed initially prior to the independent analysis of any samples. Instrumentation demonstration of capability shall be performed prior to independent sample analysis for reporting by a given method.

Initial demonstration of capability is to be performed on any sample matrix for which analyses are performed and for any cleanup procedure employed.

Anytime there is a change in staff for sample analysis or major change in instrumentation such as a column type change and for change in any cleanup procedure employed, an IDOC must be performed. (For units that have analyst rotations, once an analyst has performed an IDOC for a parameter method, the IDOC is valid for each rotation thereafter unless there is a change in the method or the instrumentation. A method change or instrumentation change requires a new IDOC.)

Method requirements for accuracy and precision for an IDOC take precedence and must be followed when an analyst performs an IDOC. North Carolina DWR WSS Laboratories SOP requirements are followed only if IDOC requirements are not specified in the method.

In the case where method-specific IDOC acceptance criteria are not specified in-house acceptance limits criteria must be developed as stated below:

1) In-house limits must be derived from a minimum of 20 results
2) Acceptance limits for recovery are set at ± three standard deviations from the mean recovery.
3) Once derived, in-house limits are to be approved and signed off on by branch supervisor and Quality Assurance coordinator.
4) If there are no existing guidelines for limits, default limits will be used until such time that twenty spike values are derived and limits can be calculated. In most instances, per cent recovery default limits for inorganic analyses will be set at 85-115% and per cent recovery limits for organic analyses at 70-130%.

In the case where method-specific acceptance criteria are not specified for IDOC evaluation, precision will be no tighter than 10% and no greater than 20% for Relative Standard Deviation (%RSD). (%RSD may be set at a higher percentage at 30% for historically difficult analyses at the discretion of the QA Coordinator or Branch Manager.)

When two methods are referenced and method-specific IDOC acceptance criteria are specified, the IDOC evaluation will adhere to the more strict method of the two.

Note: Whether using in-house limits or method-specified limits, if the IDOC study does not pass, the entire study is to be repeated. Example: Four replicates were evaluated. One of the four replicates obviously has resulted in the study failing. Four new replicate samples will need to be analyzed.
Demonstration of capability may be performed using quality control samples or other predetermined regiment for demonstration of proficiency in a given test method for those analytes that do not lend themselves to spiking**.** Each SOP should spell out the regiment for performing and evaluating an IDOC for method parameter(s).

Please reference the Quality Assurance Manual for the Division of Water Resources Water Science Section Chemistry Laboratories, Section 8.5.1 Initial Demonstration of Capability (IDOC) for procedural guidance.