Fish Tissue Monitoring Program (FTMP)

QUALITY ASSURANCE PROJECT PLAN

Program Administered and Plan Prepared by:
North Carolina Department of
Environment & Natural Resources
Division of Water Resources
Environmental Sciences Section
Intensive Survey Branch

EPA Approved
March 28, 2014
Version 1.2

Abbreviations

ISB	Intensive Survey Branch
CWA	Clean Water Act
DO	Dissolved Oxygen
DWR	Division of Water Resources
EPA	Environmental Protection Agency
ESS	Environmental Sciences Section
FDA	Food and Drug Administration
FTMP	Fish Tissue Monitoring Program
ISB	Intensive Survey Branch
NCDENR	North Carolina Department of Environment and Natural Resources
NCDHHS	North Carolina Department of Health and Human Services
NFQA	National Field Quality Assurance
NPDES	National Pollutant Discharge Elimination System
PQL	Practical Quantitation Limit
PTFE	Polytetrafluoroethylene (Teflon)
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
SFCAP	Stream Fish Community Assessment Program
SOP	Standard Operating Procedures
TMDL	Total Maximum Daily Load
USFDA	United States Food and Drug Administration
USGS	United States Geological Survey

REVISION LOG

FISH TISSUE MONITORING PROGRAM (FTMP)
QUALITY ASSURANCE PROJECT PLAN

Note: Actions older than 5 years may be removed from this record

Date Edited	Editor	Version Edited	Section Edited	Changes/updates
12/19/13	Jeff DeBerardinis	1.1	Entire Document	Division of Water Quality (DWQ) changed to Division of Water Resources (DWR). Environmental Sciences Section's organizational "units" are now called "branches". *Example: Intensive Survey Unit (ISU) changed to Intensive Survey Branch (ISB).* Fish Tissue Monitoring Program moved from the Biological Assessment Branch to the Intensive Survey Branch. Updated all headers, footers, and hyperlinks.
12/19/13	Jeff DeBerardinis	1.1	Title Page	Updated document date & version to January 2014 & Version 1.2
12/19/13	Jeff DeBerardinis	1.1	Abbreviations	Updated list of acronyms
12/19/13	Jeff DeBerardinis	1.1	A1. Signature and Approval Sheet	Updated personnel and organizational names.
12/19/13	Jeff DeBerardinis	1.1	A2. Distribution List	Updated personnel and organizational names.
12/19/13	Jeff DeBerardinis	1.1	A3. Project Organization	**Project Management and Oversight:** Updated staff duties **Table A3.1:** Updated Organizational Chart
12/19/13	Jeff DeBerardinis	1.1	A4. Problem Definition and Background	Updated organization names
12/19/13	Jeff DeBerardinis	1.1	A5, B1, B3, and References	Corrected USEPA reference year from 2007 to 2000
12/19/13	Jeff DeBerardinis	1.1	A6. Quality Objectives and Criteria	**Field & Laboratory Measurements:** Changed weight measurement criteria "to the nearest gram" (previously required: "to the nearest 0.1 gram").
12/19/13	Jeff DeBerardinis	1.1	B2. Sampling Methods	**Sample Collection:** Changed weight measurement criteria "to the nearest gram" (previously required: "to the nearest 0.1 gram").
12/19/13	Joanna Gmyr	1.1	B5. Quality Control	**Field Activities:** Updated 2nd paragraph **FTMP Laboratory Activities:** Deleted 3rd bullet – this is handled by the DWR Laboratory and is not part of the FTMP program.
12/19/13	Jeff DeBerardinis	1.1	B6. Equipment Testing, Inspection, and Maintenance	**Table B6.1** Removed maintenance requirements for YSI 85 & Accumet field meters (no longer used by program). Added maintenance requirements for YSI Professional Plus meters.
12/19/13	Joanna Gmyr	1.1	B7. Instrument Calibration and Frequency	Replaced text in this section and added more detailed description of meter calibration.
12/19/13	Jeff DeBerardinis	1.1	Appendix 1	Updated Fish Tissue Monitoring Program SOP (December 2013, Ver. 1.2)

Date Edited	Editor	Version Edited	Section Edited	Changes/updates
12/19/13	Joanna Gmyr	1.1	Appendix 4	Updated Stream Fish Community Assessment Program SOP (Dec. 2013)
12/19/13	Joanna Gmyr	1.1	Appendix 5	Updated Calibration Sheet
12/19/13	Joanna Gmyr	1.1	Appendix 6	Added Appendix 6 – Guidance Tables for YSI Professional Plus field meters.
12/2/2011	Jeff DeBerardinis	1.0	All Sections	Updated titles of staff
12/2/2011	Jeff DeBerardinis	1.0	A3	Updated name of Project Coordinator
12/2/2011	Jeff DeBerardinis	1.0	A3	Deleted “basin”. FTMP data no longer included in BARs.
12/2/2011	Jeff DeBerardinis	1.0	A3	Deleted Assistant Environmental Biologist II
12/2/2011	Jeff DeBerardinis	1.0	A5	Updated map of fish tissue monitoring sites in NC
12/2/2011	Jeff DeBerardinis	1.0	A5	Updated ISB SOP links
12/2/2011	Jeff DeBerardinis	1.0	A5. Reporting	Deleted language and map concerning Basinwide Assessment Reports. FTMP data no longer included in BARs.
12/2/2011	Jeff DeBerardinis	1.0	A6	Deleted “Tier I”
12/2/2011	Jeff DeBerardinis	1.0	A7	Updated ISB SOP link.
12/2/2011	Jeff DeBerardinis	1.0	A8	Changed “Data Report Package” to “Data Reporting”. Deleted all language concerning fish tissue data reporting in Basinwide Assessment Reports. FTMP data is no longer included in Basinwide Assessment Reports. Added FTMP data web link.
12/2/2011	Jeff DeBerardinis	1.0	B1	Deleted language concerning Basinwide Monitoring Program. FTMP data is no longer included in Basinwide Assessment Reports.
12/2/2011	Jeff DeBerardinis	1.0	B1	Deleted all “Tier 1” and “Tier II” text, and replaced with “screening” or “intensive” where appropriate.
12/2/2011	Jeff DeBerardinis	1.0	B1	Updated FTMP and ISB SOP web link.
12/2/2011	Jeff DeBerardinis	1.0	B2	Updated ISB SOP link.
12/2/2011	Jeff DeBerardinis	1.0	B5	Deleted “and/or the Assistant Environmental Biologist II”
12/2/2011	Jeff DeBerardinis	1.0	B5	Deleted “(Tier 2)”
12/2/2011	Jeff DeBerardinis	1.0	B6	Deleted “and the Assistant Environmental Biologist II are”
12/2/2011	Jeff DeBerardinis	1.0	C1	Deleted “the Assistant Environmental Biologist II”
12/2/2011	Jeff DeBerardinis	1.0	D1	Deleted “and Assistant Environmental Biologist II”
12/2/2011	Jeff DeBerardinis	1.0	D1	Deleted “and Assistant Environmental Biologist II”
12/2/2011	Jeff DeBerardinis	1.0	D3	Deleted “Basinwide Assessment Reports and”

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SECTION A:

PROJECT MANAGEMENT

A1. Signature and Approval Sheet

Approved by:

Jeff DeBerardinis
Fish Tissue Monitoring Program Coordinator
Environmental Sciences Section, NC DWR

1/9/2014
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Jason Green
Intensive Survey Branch Supervisor
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1/9/2014
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Joanna Gmyr
Quality Assurance Coordinator
Environmental Sciences Section, NC DWR

1/9/2014
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Dianne Reid
Section Chief
Environmental Sciences Section, NC DWR

1/24/2014
Date

Designated Approving Official
Environmental Protection Agency Region IV

3/28/2014
Date

A2. Distribution List

Primary Distribution:

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Andrea Zimmer, Monitoring and Information Analysis Section Chief
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Norma Good, Laboratory QA/QC Officer
Kathy Stecker, Modeling & Assessment Branch Supervisor
Kent Wiggins, Laboratory Section Chief
Ian McMillian, Basin Planning Branch Supervisor

A3. Project Organization

The Fish Tissue Monitoring Program (FTMP) is housed within the Environmental Sciences Section of the Division of Water Resources (DWR), within the North Carolina Department of Environment and Natural Resources (NCDENR). Activities associated with the FTMP (fieldwork, project management, QA, data management, analysis, and reporting) are performed by Intensive Survey Branch (ISB) staff members, with additional assistance provided by other staff in the Environmental Sciences Section (ESS).

An abbreviated organizational chart for the Division of Water Resources is provided in Figure A3.1. Information on specific individuals' roles and responsibilities follows. Phone numbers and addresses for the offices listed can be found at http://portal.ncdenr.org/web/wq

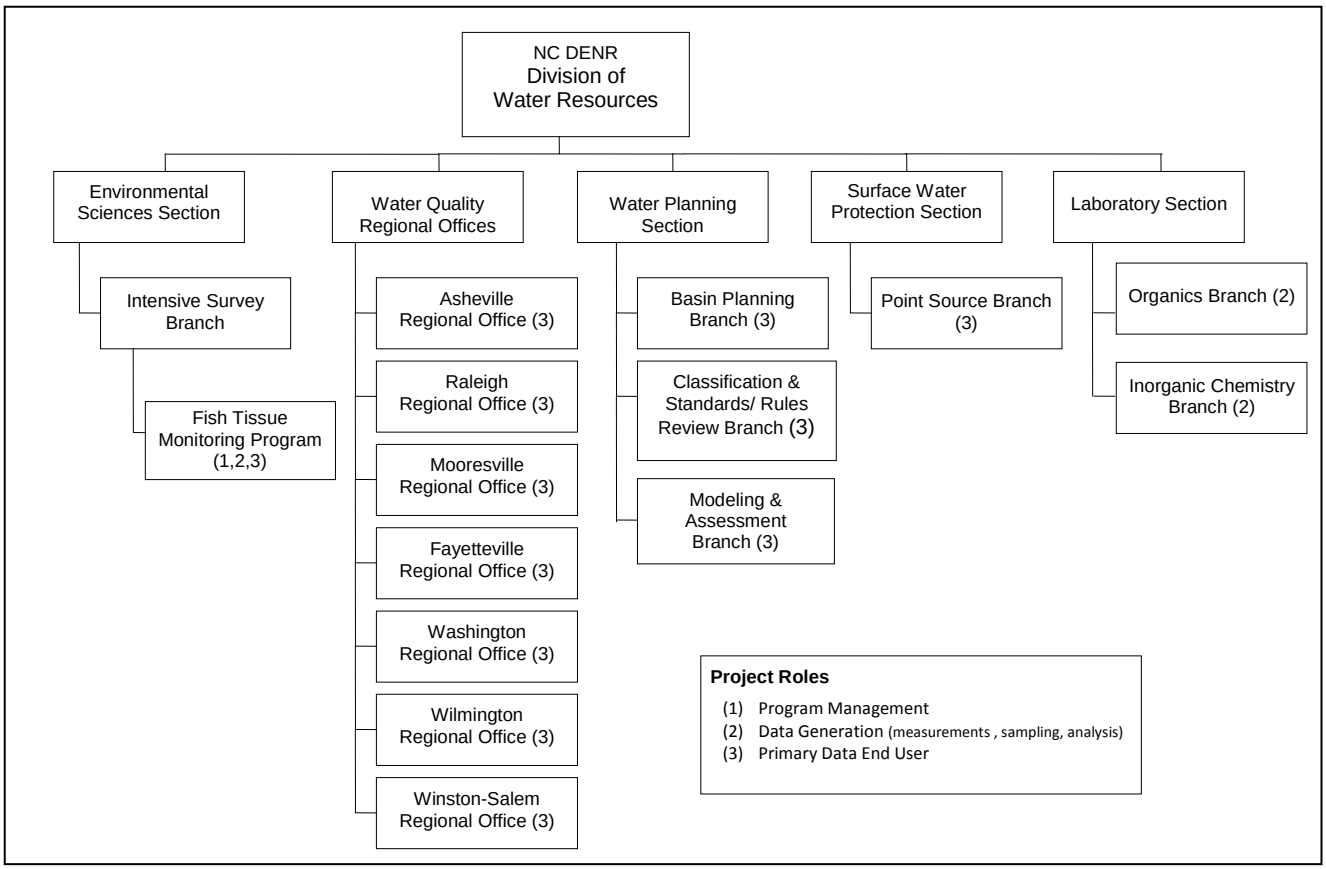

Figure A3.1 North Carolina Division of Water Resources Organizational Chart.

Project Management and Oversight

Intensive Survey Branch (ISB) Supervisor

Jason Green

Supervisor of lakes assessment and fish tissue programs. Serves as liaison between ISB and internal NC DWR customers of ISB data as well with other divisions within NCDENR, NC Department of Transportation, EPA, U. S. Geological Survey, and various nongovernmental organizations. Ensures that all FTMP activities are conducted in accordance with all pertinent QAPP's and SOP's. Recommends new employee hires and approves changes to the FTMP.

Environmental Biologist, ISB

Jeff DeBerardinis
Project Coordinator

Prepares study plans; selects sites; informs regions, agencies, and public of fish tissue studies. Trains field staff. Ensures fish tissue samples are collected and processed in accordance with the SOP. Coordinates delivery of samples to analytical laboratory. Communicates with various agencies and regional offices to identify fish tissue concerns across the State. Tracks, receives, and analyzes fish tissue results for the Division. Enters results into DWR fish tissue database. Conducts statistical and QA/QC analyses, researches literature, and maintains information files on fish contaminants. Generates special study and special request reports involving fish tissue data. Responds to information requests from other agencies and individuals.

Field Staff

Staff members of the Intensive Survey Branch and other branches within ESS assist in the sample collection and processing aspects.

Resources Assurance Coordinator

Joanna W. Gmyr
QA Coordinator, ESS

Documents QA practices of FTMP. Maintains FTMP QAPP. Develops and recommends QA/QC improvements. Ensures that the FTMP is conducted in accordance with the FTMP QAPP.

Primary Data-End-Users

NC Department of Health and Human Services (NCDHHS)

Dr. Ken Rudo, Epidemiologist, Division of Public Health
Occupational and Environmental Epidemiology

- Analyses of DWR fish tissue contaminant data
- Recommend fish consumption advisories for human heath to State Health director

Staff from the DHHS should:

- Provide input to the Environmental Biologist and Intensive Survey Branch Supervisor on changes needed to the FTMP as part of a continuous program assessment process.
- Report any data anomalies to the Environmental Biologist and ISB Supervisor.
- Report any waterbodies that are in need of assessment.

Water Planning Section

Tom Fransen, Section Chief

Supervises the Basin Planning Branch and Modeling and Assessment Branch.
These branches include numerous staff acting as primary end-users of data produced by the FTMP.

Staff from the Planning Section should:

- Provide input to the Environmental Biologist and ISB Supervisor on changes needed to the FTMP as part of a continuous program assessment process.
- Report data anomalies to the Environmental Biologist and ISB Supervisor.
- Report waterbodies in need of assessment.

Regional Offices

Regional Office Supervisors:
Corey Basinger, Winston-Salem (WSRO)
Landon Davidson, Asheville (ARO)
Jim Gregson, Wilmington (WiRO)
Belinda Henson, Fayetteville (FRO)
David May, Washington (WaRO)
Michael Parker, Mooresville (MRO)
Danny Smith, Raleigh (RRO)

There are seven regional offices within the NCDENR. The regional offices perform the Department's duties on a local level and are responsible for compliance and enforcement actions.

Staff from the regional offices should:

- Provide input to the Environmental Biologist and ISB Supervisor on changes needed to the FTMP as part of a continuous program assessment process.
- Report data anomalies to the Environmental Biologist and ISB Supervisor.
- Report waterbodies in need of assessment.

Water Planning Section
Tom Fransen, Section Chief

- Supervises the Basin Planning Branch and the Modeling & Assessment Branch. These Branches include numerous staff acting as primary end users of data produced by the FTMP.
- Staff from the Basin Planning Branch and the Modeling & Assessment Branch should:
    - Provide input to the Environmental Biologist and ISB Supervisor on changes needed to the FTMP as part of a continuous program assessment process.
    - Report any data anomalies to the Environmental Biologist and ISB Supervisor.
    - Report on any waterbodies or impacts from permitted facilities that are in need of assessment.

U. S. EPA
EPA Region IV

- Review, provide comments, and approve QAPP and subsequent revisions on behalf of EPA Region IV.
- Perform mid-year and end-of-year assessments of all DWR monitoring program, including the Fish Tissue Monitoring Program, to determine progress on tasks listed in the annual §106 grant work plan.

A4. Problem Definition and Background

Introduction

As part of funding agreements between the State and the U. S. Environmental Protection Agency (EPA) and to support the goals of the Clean Water Act (CWA), North Carolina agrees to monitor the waters of the state and report findings to the EPA. The CWA defines its objective as: " . . . *to restore and maintain the chemical, physical, and biological integrity of the Nation's waters, and, where attainable, to achieve a level of water quality that provides for the protection and propagation of fish, shellfish, and wildlife, and for recreation in and on the water*."

Because fish spend their entire lives in the aquatic environment, they incorporate chemicals from this environment into their body tissues. Contamination of aquatic resources has been documented for heavy metals, pesticides, and other complex organic compounds. Once these contaminants reach surface waters, they may be available for bioaccumulation, either directly or through aquatic food webs and may accumulate in fish and shellfish tissues. Results from fish tissue monitoring can serve as an important indicator of further contamination of sediments and surface water.

Fish Tissue Monitoring Program Objectives

The DWR utilizes several programs and tools to assess the quality of the state's waters. The primary objective of the Fish Tissue Monitoring Program is to provide fish contaminant data for waterbodies to the NCDHHS for human fish consumption, Basin Planning for Use Support, and the Planning Section for Basinwide Water Quality Management Plans. Secondary objectives of the FTMP are to provide data suitable for supporting the following DWR activities:

- Water Planning Section:
  - Biennial 303(d) and 305(b) reporting to EPA, including identification of areas of impairment or degradation,
  - TMDL development,
  - Prioritization of restoration activities, and
  - Background information for Use Attainability studies.
- Water Quality Permitting Section, Wastewater Branch:
  - Identification of background levels of constituents for determination of NPDES permit limits, and
  - Identification of dischargers causing unacceptable impacts.
- Regional Offices:
  - Background information to assist with water quality management activities in each region.

A5. Project/Task Description and Schedule

Overview

The Fish Tissue Monitoring Program (FTMP) is the primary process within NCDENR to monitor fish tissue contaminants across the state of North Carolina. The program has been in existence since the late 1970's. Its core mission is to sample accessible and publicly fished sites for the presence of fish tissue contaminants. Contamination of aquatic resources has been documented for heavy metals, pesticides, and other complex organic compounds across North Carolina. Once these contaminants reach surface waters, they may be available for bioaccumulation, either directly or through aquatic food webs, and may accumulate in fish and shellfish tissues. Results from fish tissue monitoring can serve as an important indicator of further contamination of sediments and surface water. Data generated from the program are also forwarded to the NC Department of Health and Human Services (NCDHHS) for use in posting fish consumption advisories across the State.

Approximately 500 sites, located primarily in the Piedmont and Coastal Plain, have been assessed by the FTMP (Figure A5.1). Approximately 30 sites (both new and existing) are sampled each year. Most of the stations are located at boat ramps, public access areas, lakes, reservoirs, estuaries, and/or streams accessible by boat. Wadeable and lower Strahler order rivers are also monitored but not as frequently.

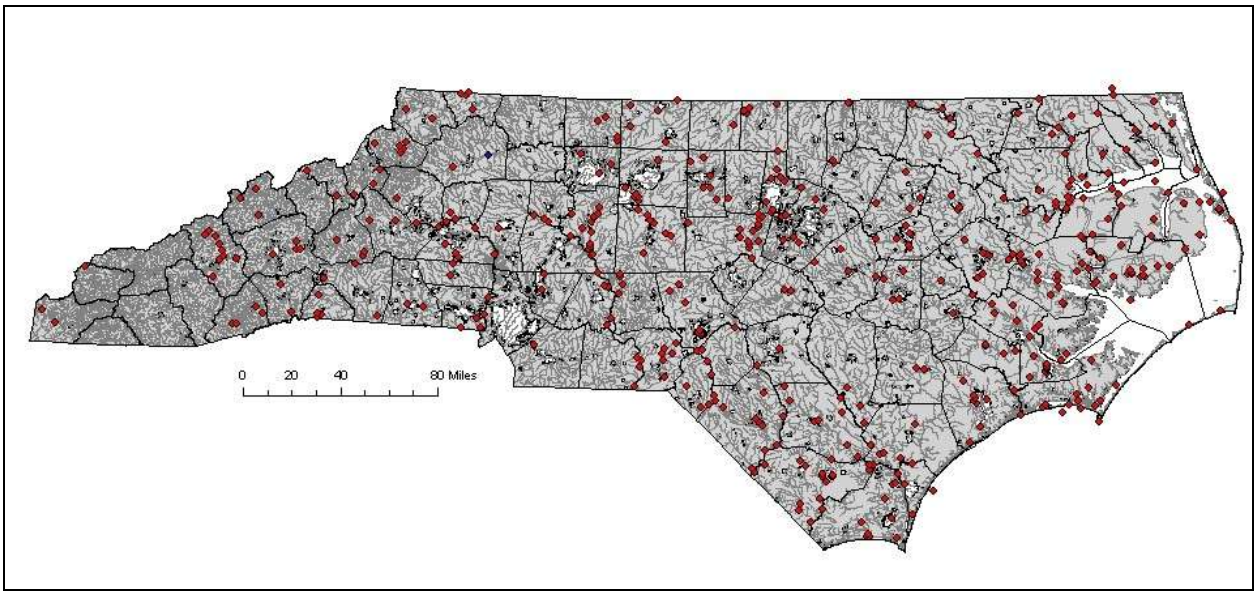

Figure A5.1 Fish Tissue Monitoring Sites, 1980 – 2013.

Fish Tissue Indicators

The FTMP evaluates fish tissue contaminants across North Carolina using guidelines described in the EPA guidance document *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories (USEPA, 2000)*. Target analytes include mercury, heavy metals, PCB's, PBDE's, and chlorinated pesticides. A list of routine FTMP target analytes is summarized in Appendix 2. In evaluating fish tissue analysis results, several different types of criteria are used. Human health concerns related to fish consumption are screened by comparing results with federal Food and Drug Administration (FDA) action levels (USFDA, 1980), Environmental Protection Agency (USEPA) recommended screening values, and criteria adopted by the North Carolina State Health Director (Appendix 1). At the request of DWR, the N.C. Division of Occupational and Environmental Epidemiology evaluates individual parameter results that appear to be of potential human health concern.

Other Water Quality Indicators
Although fish tissue contaminants are the primary tool used by the FTMP, other water quality measurements (water temperature, dissolved oxygen, pH, and specific conductance) are also monitored at every site in accordance with the ISB SOP:
http://portal.ncdenr.org/c/document_library/get_file?uuid=522a90a4-b593-426f-8c11-21a35569dfd8&groupId=38364

Sampling Schedule
Fish tissue monitoring sites are sampled yearly, usually between April and November. A yearly schedule of fish survey sites is generated from the following:

- Sites to assess mercury bioaccumulation issues,
- Special study requests from regional offices and other agencies,
- Sites where contaminant data is incomplete or absent, and/or
- Sites where contaminants have been elevated or are suspected.

Sampling Methods Overview

Fish Tissue Collection
The FTMP field and laboratory methods are described in detail in the ESS Fish Tissue Assessment SOP (Appendix 1). Additional information on sample collection activities is also available in section B2 of this document. In most cases, the FTMP employs electrofishing as the primary means of fish collection. Collections on lakes and non-wadeable streams are usually accomplished using a boat-mounted electrofisher, which is powered by a 2.5-watt or a 7.5-watt generator. Collections on wadeable streams are accomplished using backpack electrofishing techniques. Refer to the Stream Fish Community Assessment Program (SFCAP) SOP (Appendix 4) for details on this method.

Packaged fish are immediately placed on wet ice and chilled to 4°C for transport back to the ESS laboratory. Individual fish are identified to species under the supervision of an experienced biologist familiar with North Carolina fish fauna. Samples are processed by ESS staff members and either sent directly to the Division's Analytical Chemistry Laboratory (or an alternative analytical laboratory) or immediately frozen and stored at –20°C for later analysis. Turnaround times for analytical results are usually one month for metals analyses and several months for pesticide and organics analyses.

Water Quality Field Measurements
Measurements taken in the field include water temperature, pH, specific conductance, and dissolved oxygen. Field measurements are discrete and are made *in situ* by field staff at the time of the station visit. All field measurements are performed in accordance with Section III of the ISB SOP http://portal.ncdenr.org/c/document_library/get_file?uuid=522a90a4-b593-426f-8c11-21a35569dfd8&groupId=38364

Data Management
Field measurements and observations are recorded on the Fish Tissue Survey Information form (Fish Tissue SOP - Appendix B). Field data are compiled, quality assured, and entered into the FTMP electronic database. Fish tissue results are received from the analytical laboratory as hardcopy reports. Analytical results are compiled, quality assured, and entered into the FTMP electronic database. Hardcopy reporting sheets are archived at ESS for database verification. All results are warehoused in the FTMP database, which is a Microsoft Access® 2007 database. The database is updated whenever sample analyses are completed and received or when errors in previously entered data are identified.

Reporting
The primary forms of reporting within the FTMP include: Reports to the NCDHHS and other agencies, and site-specific special study reports. The information may be incorporated into Basinwide Water Quality Management Plans and required biennial reports to EPA for inventory and impairment (combined 303(d)/305(b) reporting). Data are uploaded annually to the ISB's web page for public dissemination.

Tissue results are used for Biennial 303(d) and 305(b) reporting to EPA, including identification of areas of impairment or degradation. Impairment can lead to further actions by other DWR programs, such as intensive studies, development of TMDLs or other strategies, and implementation of additional pollutant controls.

Reports to NCDHHS and Other Agencies
ESS fish tissue results are reported to the NCDHHS and other state agencies *via* formal reports and internal memoranda. These reports are approved by the ISB Supervisor and the ESS Section Chief and kept on file at the ESS laboratory.

Special Study Reports
Results of special studies are summarized in formal reports and internal memoranda. These reports are approved by the ISB Supervisor and the ESS Section Chief and forwarded to the appropriate party or regional office staff. Copies are kept on file at the ESS laboratory.

A6. Quality Objectives and Criteria

Components of a quality assurance and quality control plan are described in the Fish Tissue Assessment SOP (Appendix 1). All investigations conducted by the FTMP follow a written study plan that is approved before the actual sampling is conducted. The FTMP QAPP addresses activities that are conducted by the FTMP on a regular basis. Fish tissue samples are collected and prepped by the FTMP. The samples are then sent to the Division's Analytical Chemistry Laboratory for analytical analyses, which are beyond the scope of the FTMP QAPP and are regulated by the Quality Assurance Manual for the NC Division of Water Resources Laboratory Section (Appendix 3).

Bias

The FTMP is conducted according to a non-random sampling design; therefore, bias will exist due to site locations (i.e., sites that can be safely accessed by boat or by the sampling crew while wearing a backpack electrofisher).

Other sources of bias include:

- Sampling is performed under existing flow and water clarity conditions. Ideally, monitoring is conducted under low to normal flow conditions with clear or slightly turbid water clarity. Sampling is not conducted if the water is so turbid that fish cannot be seen or if the water level is so high or swift that sampling would jeopardize the safety of the staff.
- Almost all sites are located within the vicinity of boat ramps and bridge crossings for ease of access and to avoid trespassing on private property.
- Target fish are of the size range normally caught by most fishermen. Small and very large fish are released or not targeted.

Using consistent sampling and laboratory methods and data analyses as describe in the Fish Tissue Assessment SOP (Appendix 1) minimizes bias from other sources.

Representativeness

The primary selection criterion for target species is to choose those commonly caught and consumed locally and of harvestable size. In freshwater ecosystems, one bottom feeding and one predator fish species should be collected. In estuarine/marine ecosystems, either one bivalve species and one finfish species or two finfish species should be collected. Generally, at least ten individuals of each target species are collected. The survey method involves sampling a tiny fraction of the fish population present at a site and may or may not completely represent the variability of pollutants in the population.

Field and Laboratory Measurements

Individual fish are identified, measured and weighed at the ESS laboratory to ensure accuracy. Total length is measured to the nearest centimeter on a standard Wildco® measuring board. The total weight of each fish is measured to the nearest gram on an electronic scale.

In the field and laboratory, taxonomic keys listed in the "References" section of the Stream Fish Community Assessment Program SOP (Appendix 4) are used to ensure consistent and accurate identification of fish species. Target species lists are generated from the DWR Fish tissue database using species data from previous sampling trips.

Single measurements of water temperature, dissolved oxygen, specific conductance, and pH are made with calibrated meters. The measurements are taken just below the stream surface. No effort is made to determine spatial or temporal variability in the measurements at a specific site.

Comparability

Fixed station locations and the Fish Tissue Assessment SOP (Appendix 1) ensure that comparable samples are taken at each site visit. Deviations from the SOP or from the written study plan due to unusual sampling situations are documented in the appropriate report or memorandum. Calibration procedures ensure accuracy and comparability of water quality measurements. To assess total variability, duplicate samples are prepared from at least 10% of the fish samples. Sample duplicates are prepared using tissue from the same fillet or composite homogenate. Duplicates are assigned a "dummy"

sample identification, which is recorded in the processing laboratory log. The analytical laboratory does not receive this information.

During intensive studies, portions of at least 10% of the prepared homogenates will be frozen at -20°C and archived at the Division's Water Resources Laboratory for a period of at least 6 months after completion of the study. This is done in case of analytical problems or the need for future references.

Completeness

It is expected that some sites will not be sampled due to problems such as inclement weather, poor water clarity, extremes in flows, equipment malfunctions, vacant positions, and staffing during the field season. As many sites as possible are sampled during the field season given existing staffing resources.

A7. Special Training/Certification

Field Staff

Fieldwork for the FTMP is normally conducted by a staff of two or three, of which one trained biologist is the lead investigator. The Environmental Biologist requires considerable knowledge of biological communities, aquatic ecosystems, and the interactions of chemical characteristics with biology as they relate to water quality. The Environmental Biologist should have graduated from a four-year college or university with a major in biology, environmental science, ecology, or a related natural science curriculum. The Environmental Biologist should be trained in meter use and calibration according to Section III of the ISB SOP: (http://portal.ncdenr.org/c/document_library/get_file?uuid=522a90a4-b593-426f-8c11-21a35569dfd8&groupId=38364). The Environmental Biologist should also be experienced in boat handling and boating safety. All staff involved in electrofishing activities should be trained in First Aid and CPR and should be familiar with standard electrofishing safety procedures. Annual recertification in First Aid and CPR is recommended.

FTMP samples are collected under the following annual collection permits:

- Scientific/Educational Collection Permit from the NC Division of Marine Fisheries and
- Collecting License and Endangered Species Permit from the North Carolina Wildlife Resources Commission's Division of Inland Fisheries.

There is currently no formal documentation of training, but field staff members are assessed on an ongoing basis by the Environmental Biologist to ensure field staff members are performing activities in accordance with all pertinent SOP's and the FTMP QAPP.

Laboratory Staff

All fish samples are prepped at the ESS laboratory under direct supervision of the Environmental Biologist according to Section 3.4 of the Fish Tissue Assessment SOP (Appendix 1). The Division's Analytical Chemistry Laboratory staff is trained according to the Quality Assurance Manual for the North Carolina Division of Water Resources Laboratory Section (Appendix 3).

A8. Documentation and Records

Quality Assurance Information, SOP, and Other Support Documentation

Once all approval signatures have been obtained, the QA Coordinator will electronically distribute copies of the approved QAPP to persons on the distribution list in Section A2 of this document. Copies must be disseminated within 30 days of final approval. The original hardcopy with approval signatures will be kept on file in the QA Coordinator's office in the ESS building. Field staff and new employees are provided a copy of the QAPP from the Environmental Biologist.

The QA Coordinator is to be notified of changes made to the SOP or any other documentation referenced by this QAPP. The QA Coordinator will be responsible for distributing the information, as described above. The QA Coordinator will also be responsible for maintaining current copies of all documents directly associated with the FTMP.

Field staff members that regularly assist in FTMP activities are responsible for reviewing the FTMP QAPP annually. The Environmental Biologist will maintain documentation of staff review of the FTMP QAPP.

The FTMP is an ongoing project; therefore, this QAPP will be reviewed on at least an annual basis. If appropriate, any changes or updates will be made as part of the annual review; however, critical revisions may be made at any time. The QA Coordinator is responsible for completing revisions, obtaining signatures of approval, and disseminating the revised document to those on the distribution list within 30 days of final approval. The version or revision number and date shall be easily identifiable by the document control information on each page. A complete list of all revisions/updates will be provided with each annual update.

Project Records

Hardcopies of the following records are maintained for at least five years in the Environmental Biologist's office:

- Study Plans
- Fish Tissue Survey Information Forms (Fish Tissue SOP - Appendix B)
- Fish Tissue Raw Data Sheets (Fish Tissue SOP - Appendix A)
- Meter Calibration Sheets (Appendix 5)
- Analytical Laboratory Reports
- Special Study Memoranda
- Reports to NCDHHS and other agencies

Electronic Data Storage

All field and laboratory measurements and analytical data are ultimately warehoused in the Fish Tissue Assessment database (Microsoft Access® 2007). A copy of the database exists on ISB's drive on the ESS server. Tape backups are run daily on the ESS servers. The database is updated on an as-needed basis whenever samples are completed or whenever errors in previously entered data are identified. Details of electronic data management and warehousing methods are further described in Section B10 of this document.

Data Reporting

All available historic and current raw data, station visit comments/observations, and station information, including HUC8digit, latitude, an longitude are stored electronically in the Fish Tissue Assessment database. All fish tissue data are made publically available via the ESS website at http://portal.ncdenr.org/web/wq/ess/ISB/fish-tissue-data Raw and analyzed fish tissue data are also provided to staff from other state and federal agencies, private consultants, academia, municipalities, private citizens, etc. via special study reports and on the ESS web site.

SECTION B:

DATA GENERATION AND ACQUISITION

B1. Sampling Process Design

The FTMP is the primary process within NCDENR to monitor fish tissue contaminants across the State. The program has been in existence since the late 1970's. Its core mission is to sample accessible and publicly fished sites for the presence of fish tissue contaminants. Sites are assessed as part of regional or watershed-specific special studies.

A detailed sampling plan is developed by the Environmental Biologist and approved by the ISB Supervisor prior to initiating any studies. At minimum, a study should involve a two-tiered approach:

- Screening studies, identify sites where commonly consumed fish species are contaminated with target analytes and may pose a risk to human health.
- Intensive studies characterize the magnitude and geographical extent of contamination in harvestable fish at sites identified in screening studies. Intensive studies should be designed to verify results of screening studies.

Target Species

The primary selection criterion for target species is to choose those that are commonly consumed locally and are of harvestable size. In freshwater ecosystems, one bottom feeding and one predator fish species are collected. In estuarine/marine ecosystems, either one bivalve species and one finfish species or two finfish species are collected. Second and third choice target species are selected in the event that the recommended target species are not collected at the site. Generally, at least ten individuals of each target species are collected.

Sample Type

To ensure even distribution of contaminants throughout tissue samples and to facilitate extraction and digestion of samples, the fillets from individual fish must be ground and homogenized prior to analysis. The fillets from an individual fish may be ground and homogenized separately or combined, depending on the analytical requirements and the sample size. Composite samples are homogeneous mixtures of samples from at least four but no more than ten individual fishes of the same species collected at a particular site during the same time period and analyzed as a single sample. Fish used in a single composite should be of similar size such that the smallest individual in a composite is no less than 75 percent of the total length (size) of the largest individual. Final individual or composite samples should be composed of at least 100 g of tissue to ensure an adequate amount of material for analysis.

Site Locations

Sites are established at publicly accessible, fixed locations (i.e., specific latitude and longitude), generally near boat ramps, public access areas, lakes, reservoirs, estuaries, and streams accessible by boat. Wadeable and lower Strahler order rivers are also monitored. Locations and their geo-references are identified using handheld GPS units or Maptech Terrain Navigator ® software. Stations are strategically located to monitor a specific area of concern such as:

- Mercury bioaccumulation issues,
- Survey requests from regional offices and other agencies,
- Sites where contaminant data is incomplete or absent, or
- Sites where contaminants have been elevated or are suspected.

A current listing of FTMP sample sites is located at http://portal.ncdenr.org/web/wq/ess/ISB/fish-tissue-data.

Adjustments to site locations and sampling regimens may be made with sufficient reason, such as:

- Safety concerns of field staff,
- Changes to location accessibility,
- Reason for sampling is no longer valid (i.e., a discontinued discharge),
- Emergence of new water quality concerns, or
- Resource constraints, particularly staff vacancies.

If any of these concerns arise, the Environmental Biologist will meet with the ISB Supervisor to determine if it is appropriate for sampling activities at the site to be discontinued.

Indicators Measured

The FTMP evaluates fish tissue contaminants across North Carolina using guidelines described in the EPA guidance document *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories (USEPA, 2000)*. The program routinely evaluates those contaminants listed in Appendix 2. Contaminants in fish tissue are measured according to Section 5 of the Quality Assurance Manual for the North Carolina Division of Water Resources Laboratory Section (Appendix 3).

All other field measurements (water temperature, pH, specific conductance, and dissolved oxygen) are conducted in accordance with the ISB SOP: http://portal.ncdenr.org/c/document_library/get_file?uuid=522a90a4-b593-426f-8c11-21a35569dfd8&groupId=38364 . Field measurements are performed to monitor environmental conditions at a site during sampling and to provide additional information related to catch rates, species present, and electrofisher settings.

Sampling Frequency

The FTMP conducts fish tissue sampling in all of North Carolina's physiographic provinces (Figure B1.1) in both wadeable and non-wadeable waters. Approximately 25 to 30 sites are sampled annually. Watershed-specific special study sites are usually sampled only once and may be sampled at any time between March and October.

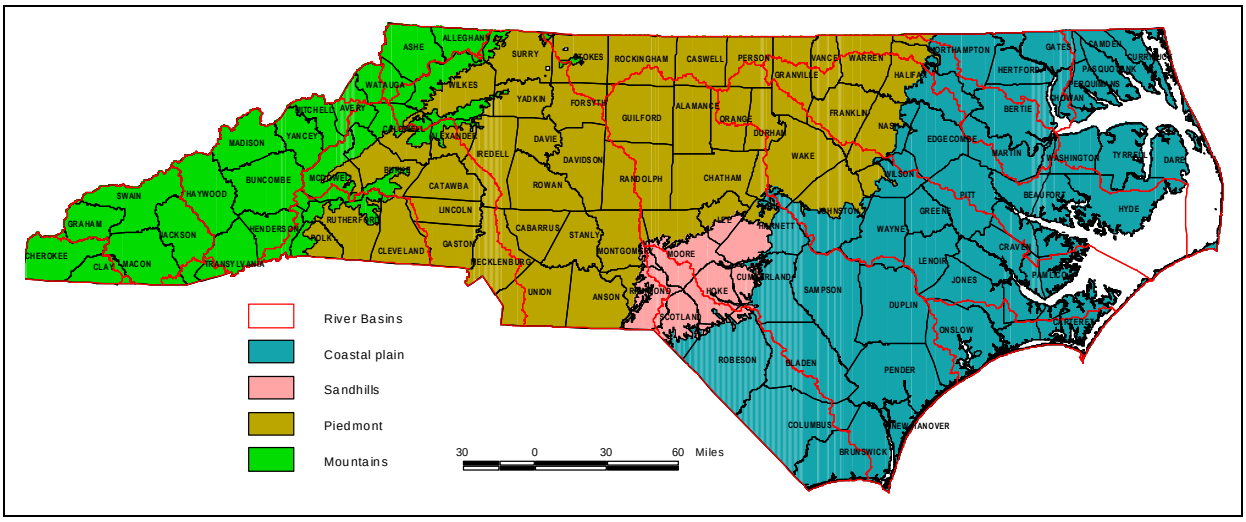

Figure B1.1 Physiographic Regions and River Basins in North Carolina.

B2. Sampling Methods

Sample Collection

Methods for collecting fish tissue samples are described in Sections 3.2 and 3.3 of the Fish Tissue Assessment SOP (Appendix 1). In most cases, the FTMP will employ electrofishing as the primary means of fish collection. Collections on lakes and non-wadeable streams are usually accomplished using a boat-mounted electrofisher powered by a 2.5-watt or a 7.5-watt generator. Collections on wadeable streams are accomplished using backpack electrofishing techniques described in the Stream Fish Community Assessment Program SOP (Appendix 4). Fish are packaged and placed immediately on wet ice and chilled to 4°C for transport back to the ESS laboratory.

Upon arrival at the ESS laboratory, fish are inspected for condition, measured and weighed to the nearest centimeter and gram respectively, and processed according to Section 3.4 of Appendix 1.

Other water quality measurements collected in the field include water temperature, pH, specific conductance, and dissolved oxygen. All field parameter measurements are performed in accordance with Section III of the ISB SOP (http://portal.ncdenr.org/web/wq/ess/ISB).

In addition to the ISB SOP citations in Table B2.1, the instruction manual for the appropriate meter should also be consulted.

Table B2.1 Field Measurement Method References and Reporting Levels.
Adopted from the Intensive Survey Branch's SOP (http://portal.ncdenr.org/web/wq/ess/ISB).

Parameter	NC DWR's Intensive Survey Branch's SOP & Section	EPA method	Reported to Nearest
Dissolved oxygen	III.3	360.1	0.1 mg/L
pH	III.4	150.1	0.1 s. u.
Water temperature	III.1	170.1	0.1 ºC
Specific conductance	III.5.2	120.1	1 µmhos/cm

Any irregularities or problems encountered by field staff members are communicated to the Environmental Biologist and the ISB Supervisor who assess the situation, consult with other project personnel if needed, and recommend a course of action for resolution. Deviations from these procedures due to unusual sampling situations shall be documented in the appropriate report or memorandum.

Composite Sampling

All samples are prepared under controlled conditions at the ESS laboratory. Composite samples are homogeneous mixtures of samples from at least four but no more than ten individual fishes of the same species collected at a particular site during the same time period and analyzed as a single sample. Specimens used in a single composite should be of similar size such that the smallest individual in a composite is no less than 75 percent of the total length (size) of the largest individual. Final individual or composite samples should be composed of at least 100 g of tissue to ensure an adequate amount of material for analysis.

B3. Sample Handling and Custody

All samples are to be handled by the Environmental Biologist and in accordance with Section 3.3 of the Fish Tissue Assessment SOP (Appendix 1). Whole fish samples are returned to the ESS Laboratory, and the sample information is recorded on the Fish Tissue Raw Data Sheet (Fish Tissue SOP - Appendix A). These datasheets are stored in the Environmental Biologist's office in a 3-ring binder labeled "Field Data Sheets". Samples that cannot be processed within 48 hours are frozen as whole fish, delivered to the ESS laboratory as soon as possible, and stored at -20°C in a locked freezer located in the fish-processing lab until processing can be performed. Tissue samples are stored according to the guidelines in Table B3.1.

Table B3.1 Recommended Container Materials and Preservation of Fish Tissue Samples
From receipt at sample processing laboratory to analysis (USEPA, 2000).

Analyte	Matrix	Sample Container	Preservation
Mercury	Tissue (fillets and edible portions, homogenates)	• Plastic, • Borosilicate Glass, • Quartz, or • PTFE	Freeze at ≤ -20°C
Other Metals	Tissue (fillets and edible portions, homogenates)	• Plastic, • Borosilicate Glass, • Quartz, or • PTFE	Freeze at ≤ -20°C
Organics	Tissue (fillets and edible portions, homogenates)	• Borosilicate Glass, • PTFE, • Quartz, or • Aluminum Foil	Freeze at ≤ -20°C
Metals and Organics	Tissue (fillets and edible portions, homogenates)	• Borosilicate Glass, • Quartz, or • PTFE	Freeze at ≤ -20°C

PTFE = polytetrafluoroethylene (Teflon)

Collection Number

After inspection and acceptance at the ESS laboratory, each FTMP sample is assigned a unique number. The tracking number includes the year and is consecutive during the period from January 1 to December 31. This number is recorded on the Fish Tissue Raw Datasheet (Fish Tissue SOP – Appendix A) to ensure sample integrity and as a means to track sample disposition.

B4. Analytical Methods

All analytical analyses of fish tissue samples are conducted by the Division's Analytical Chemistry Laboratory (or an alternative analytical lab, when necessary). Analytical lab procedures are conducted in accordance with the Quality Assurance Manual for the North Carolina Division of Water Resources Laboratory Section (Appendix 3). Turnaround times for analytical results are usually one month for metals analyses and several months for pesticide and organics analyses.

B5. Quality Control

Field Activities
Fish samples are collected and handled in the field under the supervision of the Environmental Biologist. Fish collected for analyses are shipped to the processing laboratory in such a manner as to prevent decomposition or contamination as described in Section 3.3 of the Fish Tissue Assessment SOP (Appendix 1).

Field water quality instruments are calibrated for each sampling trip prior to that day's work. Meter calibrations for dissolved oxygen (DO), pH, and specific conductance are checked after each sampling event to confirm that significant drift has not occurred and that the data collected is accurate and representative.

FTMP Laboratory Activities
The following components of the quality assurance and quality control plan for sample processing are described in Section 3.5 of the Fish Tissue Assessment SOP (Appendix 1):

- Prepare duplicate samples of at least 10% of fish samples and submit to analytical lab for analyses.
- For Intensive Studies, freeze and archive 10% of prepared homogenates for at least 6 months after study is completed.

Analytical Laboratory Activities
Components of the analytical laboratory quality assurance and quality control plan are described in the Quality Assurance Manual for the North Carolina Division of Water Resources Laboratory Section (Appendix 3).

B6. Equipment Testing, Inspection, and Maintenance

A routine preventative maintenance program minimizes the occurrence of instrument and equipment failures. Preventative maintenance is limited because most of the sampling and measuring equipment is electronic (i.e., no movable parts to repair). As a result, most repairs occur when the equipment no longer functions.

The Environmental Biologist is responsible for regular cleaning, inspection, and maintenance of their assigned equipment. All equipment should be visually inspected at each site for damage or dirt and repaired or cleaned before use. Required maintenance is shown in Table B6.1. Operators' manuals for all equipment should be consulted for manufacturer's recommendations for inspection, maintenance, and repair.

Table B6.1 Water Quality Field Instrumentation Maintenance.

Equipment	Task	Frequency
YSI Professional Plus meter	Check battery level	Daily
	Check GLP files to confirm correct calibration	Daily
	Inspect membrane for holes, tears, bubbles, fouling or other damage	Daily
	Inspect glass bulb for scratches, fouling or other damage	Daily
	Replace membrane and KCl solution	As needed if damaged, DO not calibrating or calibrations do not hold, responding slowly, showing excessive drift, or providing erratic readings
	Inspect gold cathode	As needed, when replacing membrane
	Clean cathode	As needed, if tarnished or plated
	Replace pH probe	As needed if damaged, pH not calibrating or calibrations do not hold, responding slowly, showing excessive drift, or providing erratic readings

B7. Instrument Calibration and Frequency

Water Quality Field Instrumentation

All field meters are to be inspected and calibrated at a minimum at the beginning and end of each day used. Field staff should record calibration information on the Water Quality Monitoring Field Meter Calibration Sheet form (Appendix 5) including staff name, date/time of initial calibration and post-sampling check, and meter number. Calibration procedures are documented in the ESS's meter guidance tables (Appendix 6) and in the manufacturers' instruction manuals. DO meters should be calibrated using the air calibration method.

Standards should be selected so that they bracket the range of measurements expected that day. Traceable pH buffers (standards) and specific conductance standards are purchased by the ISB. Specific conductance is typically calibrated with a 1,000 µS/cm standard first, then calibration is verified with a 500 µS/cm standard. Meters currently in use require pH standards of 4.0, 7.0, and/or 10.0 S.U.

Meters should also be checked against standards periodically throughout the day and recalibrated if needed if any of the following occur:

- physical shock to meter;
- DO membrane is touched, fouled, or dries out;
- unusual (high or low for the particular site) or erratic readings, or excessive drift;
- extreme readings (e.g., extremely acidic or basic pH; D.O. saturation >120%);
- measurements are outside of the range for which the meter was calibrated.

A post-sampling check is completed at the end of each sampling day to confirm significant drift has not occurred and that readings are accurate and representative. If post-sampling check readings are not within the acceptable QC ranges (DO= ±0.5, Specific conductance= 10%, pH=±0.2) or a post-sampling check is not completed, data are determined questionable and should be discarded.

All samples are weighed on balances that are properly calibrated and of adequate accuracy and precision to meet program data quality objectives. Balance calibration should be checked at the beginning of each weighing session.

B8. Inspection/Acceptance for Supplies and Consumables

All instruments, work surfaces, and containers used to process samples are made of materials that can be easily cleaned and are not themselves potential sources of contamination. Equipment used in processing samples for organics analyses is composed of stainless steel, anodized aluminum, borosilicate glass, polytetrafluoroethylene (PTFE), or ceramic. Equipment used in processing samples for metals analyses is composed of high-quality corrosion-resistant stainless steel (when nickel and chromium are not analytes of concern), PTFE, ceramic, polypropylene, or polyethylene. The Environmental Biologist is responsible for the procurement and maintenance of all equipment and consumables associated with the FTMP.

B9. Acquired Data (Non-Direct Measurements)

All data will be generated through the FTMP field activities and subsequent laboratory analyses, with two exceptions:

- Geo-referenced (latitude and longitude) data are obtained from Maptech Terrain Navigator® software or from a Garmin GPS meter.
- Target species lists are generated from the DWR Fish tissue database using species data from previous sampling trips.

Both datasets are used for planning and site characterization before site visits.

B10. Data Management

Data from the Fish Tissue Survey Information Sheets and analytical laboratory reports are manually keyed into the Fish Tissue Assessment database (Microsoft Access® 2007) by the Lead Environmental Biologist. The Environmental Biologist reviews the data for completeness, errors, unlikely or impossible values, *etc*. Questionable records are checked against hard copy raw data and laboratory sheets kept on file at ESS.

Analytical data reported below the method detection limit, including a datum reported as *Not Detected* or *No Observed Response*, is assigned a value of one-half the Practical Quantitation Limit (PQL). The PQL serves as a practical and routinely achievable detection limit. A datum reported at or above the PQL is used as reported. The following statistics are calculated for each sampled species at each site:

- Range of target analyte concentrations,
- Arithmetic mean of target analytes,
- Standard deviation of mean target analyte concentrations, and
- Number of samples.

Data are kept current and correct through tools such as update and append queries within the database, input requirements built into the software, and through frequent searches and analyses. Copies of the database reside on the ESS server. Tape backups are run daily on the ESS servers. The database is updated on an as-needed basis when samples are completed or when errors in previously entered data are identified. Hardcopy field data and reporting sheets are archived at ESS for database verification.

SECTION C:

ASSESSMENT AND OVERSIGHT

C1. Assessments and Response Actions

The Environmental Biologist is responsible for the FTMP and serves as the coordinator and the liaison between the program, the ISB, the ESS, the Basin Planning Branch, and other data users. All laboratory work, including fish handling and processing, is conducted by the Environmental Biologist or trained ESS staff members who are familiar with all pertinent SOP's. All laboratory work is conducted in accordance with the current SOP and under the direct supervision and guidance of the Environmental Biologist. Issues with any aspect of the program are immediately reported to the Environmental Biologist, who will assess the issue, consult with the ISB Supervisor and other associated parties, and determine the appropriate course of action.

Annually, all field staff participate in USGS's National Field Quality Assurance (NFQA) Program. The NFQA is a yearly proficiency test for pH and specific conductance. Staff who do not receive satisfactory results are provided additional field meter training and retested. The QA Coordinator oversees the NFQA program for ESS.

C2. Reports to Management

The Environmental Biologist reports monthly on the status of FTMP projects *via* staff meetings, internal memoranda, and e-mail correspondence. Reports are submitted to the ISB supervisor and/or ESS Section Chief. FTMP activities are also included in the monthly ESS Update.

The Environmental Biologist maintains documentation of all changes made to FTMP databases as well as changes to tissue criteria, SOP's, and field procedures. All program changes and modifications are conveyed to the ISB supervisor as needed.

SECTION D:

DATA VALIDATION AND USABILITY

D1. Data Review, Verification, and Validation

Data verification and validation occurs at every step of data generation and handling. The Environmental Biologist and assisting staff are responsible for verifying that all records and results produced or handled are completely and correctly recorded, transcribed, and transmitted. The Environmental Biologist also responsible for ensuring that all activities (sampling, measurements, and analyses) comply with all requirements outlined in the FTMP QAPP and SOP. The Environmental Biologist is responsible for final verification and validation of all results.

Invalid sample data are not used in the FTMP. The data are considered invalid if the sample was:

- Collected or handled under suspect conditions (e.g., samples collected by untrained staff or where the methods could not be verified),
- Collected and handled according to methods that do not conform to all pertinent SOP's,
- Contaminated during collection or handling, or
- Not properly preserved and/or handled, resulting in deteriorated specimens.

Sample data are also considered invalid if post-sampling meter calibrations for dissolved oxygen (DO), pH, and specific conductance are beyond acceptable limits (DO = $\pm$0.5; pH = $\pm$0.2; conductivity = $\pm$10%). If meter calibrations are not within the acceptable limits, the data are discounted and are not entered in the database.

Data are kept current and correct through tools such as update and append queries within the database, input requirements built into the software, and through frequent searches and analyses. Copies of the database reside on the ESS server. Tape backups are run daily on the ESS servers. The database is updated on an as-needed basis when samples are completed or when errors in previously entered data are identified. Hardcopy field data and reporting sheets are archived at ESS for database verification.

D2. Validation and Verification Methods

The Environmental Biologist reviews all results to ensure accuracy and completeness. Questionable records are checked against and compared to hardcopies of raw data and laboratory sheets kept on file at ESS. When necessary, field and analytical laboratory staff are contacted to verify data records.

A datum reported below the method detection limit, including a datum reported as *Not Detected* or *No Observed Response* will be assigned a value of one-half the Practical Quantitation Limit (PQL). The PQL serves as a practical and routinely achievable detection limit. A datum reported at or above the PQL will be used as reported.

D3. Reconciliation with User Requirements

After the data have been analyzed and summarized, results from the program are communicated *via* ESS Chief-approved internal, site-specific memoranda.

Statistical validation methods are not used to determine possible anomalies or outliers of the data.

Any issues encountered in meeting the performance criteria as stated in Section A6 of this document (or limitations in the use of data) are documented in the final report.

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APPENDIX 1:

FISH TISSUE ASSESSMENTS
STANDARD OPERATING PROCEDURES (SOP)

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STANDARD OPERATING PROCEDURES

FISH TISSUE ASSESSMENTS

NORTH CAROLINA
DEPARTMENT OF ENVIRONMENT
and NATURAL RESOURCES
Division of Water Resources
Environmental Sciences Section
Intensive Survey Branch

December, 2013
Version 1.2

Standard Operating Procedures
Fish Tissue Assessments

Environmental Sciences Section
Intensive Survey Branch

NORTH CAROLINA DEPARTMENT OF ENVIRONMENT
AND NATURAL RESOURCES
Division of Water Resources

This report has been approved for release:

12/20/13

Jason Green
Supervisor, Intensive Survey Branch

Date

1/6/2014

Dianne Reid
Chief, Environmental Sciences Section

Date

REVISION LOG

Date Edited	Editor	Version Edited	Section Edited	Changes/updates
12/19/13	Jeff DeBerardinis	Ver. 1.1, Dec. 2011	Cover Page	Updated cover photo
12/19/13	Jeff DeBerardinis	Ver. 1.1, Dec. 2011	All Sections	Changed Division of Water Quality (DWQ) to Division of Water Resources (DWR) throughout
12/19/13	Jeff DeBerardinis	Ver. 1.1, Dec. 2011	All Sections	Changed Biological Assessment Unit to Intensive Survey Branch throughout to reflect reorganization
12/19/13	Jeff DeBerardinis	Ver. 1.1, Dec. 2011	Cover page	Prior approval version date changed from December 2011 to December 2013, version changed from 1.1 to 1.2
12/19/13	Jeff DeBerardinis	Ver. 1.1, Dec. 2011	Signature Page	Approval signatures updated
12/19/13	Jeff DeBerardinis	Ver. 1.1, Dec. 2011	3.4	Changed weight measurement criteria "to the nearest gram" *(previous criteria: "to the nearest 0.1 gram").*
12/19/13	Jeff DeBerardinis	Ver. 1.1, Dec. 2011	3.6	Corrected EPA dioxin SV from 0.7 ppt to 0.26 ppt
12/19/13	Joanna Gmyr	Ver. 1.1, Dec. 2011	Appendices 1&2	Changed reference format to Appendices A & B (previously referred to as Appendices 1 &2) Also updated in-text references accordingly.
12/01/2011	Jeff DeBerardinis	Ver. 1.0, June 2006	Introduction	Prior approval version date changed from January 1997 to June 2006
12/01/2011	Jeff DeBerardinis	Ver. 1.0, June 2006	3.6	NC Health director selenium limit updated from 5µg/g to 10 µg/g. (limit changed in 2007)
12/01/2011	Jeff DeBerardinis	Ver. 1.0, June 2006	Table 1.	EPA screening value for mercury updated from 0.4 ppt to 0.3 ppt. NC Health director selenium limit updated from 5µg/g to 10 µg/g. (limit changed in 2007)
12/01/2011	Jeff DeBerardinis	Ver. 1.0, June 2006	Appendix 1.	Fish tissue raw data sheet replaced with new version.

INTRODUCTION

It is the purpose of this manual to provide details on standard operating procedures of the Intensive Survey Branch of the Division of Water Resources (DWR) for the collection and analysis of fish tissue data. Consistency in data collection and analysis is the cornerstone for evaluating biological integrity. The procedures provided in this manual are a synthesis of widely used methods and methods developed from the experience of personnel within the branch. These methods have been shown to provide repeatable and useful data for water quality evaluation.

This manual will be reviewed regularly and revised as necessary. The prior approved version of this manual was dated December 2011. All current employees and new employees within the branch will be provided with this manual to serve as a guideline of the branch's activities, methods, and procedures. Revisions of this manual will be provided to each employee and it will be the responsibility of the employee to keep his or her manual current.

The standard operating procedures (SOP) and quality control procedures (QC) in this manual will be the basis for all fish tissue monitoring in the waters of North Carolina, and the subsequent data provided in memoranda and reports prepared by the Intensive Survey Branch. Deviations from these procedures for unusual sampling situations shall be documented in the appropriate report or memorandum.

1.0 SAFETY PROGRAM

The Intensive Survey Branch is required to sample throughout North Carolina at times and places where medical facilities may not be readily available. It is imperative that all employees are instructed in and follow safety precautions when using sampling equipment and hazardous materials. The Environmental Sciences Section has a Safety Committee which is responsible for maintenance and development of current safety procedures. The Committee also maintains the safety standard operating procedures document with which all personnel should be familiar. In addition, all personnel involved in electrofishing activities should be trained in First Aid and CPR and should be familiar with standard electrofishing safety procedures.

Sampling conditions are the primary safety factor to be considered for field work. If any field conditions, such as high flows or thunderstorms, raise the question of whether a sample can be safely collected, then decisions should always be made with the safety of personnel of prime concern. This same concern for safety of staff must be of primary importance when scheduling the amount of time to be spent in the field. Long days combined with strenuous effort increase the probability of accidents occurring. "**Safety first**" must always be the rule.

Employees should promptly report on-the-job accidents to their supervisor. If an accident occurs during field operations, the first responsibility of the team leader is to get first aid treatment for the injured employee; their second responsibility is to promptly notify their supervisor. The Safety Committee maintains a written record of accidents.

2.0 STUDY PLANS

All investigations conducted by the Intensive Survey Branch will follow a written study plan including but not limited to the:

- **Introduction** - Will identify the nature and history of the area being investigated and the person or agency requesting the study.

- **Objectives** - The purpose of the investigation and expected accomplishments.

- **Sampling Location Selection** - Locating sampling points is of extreme importance in the initiation of fish tissue monitoring. The variables in watersheds are many and should be considered in as much detail as possible before sites are selected to monitor any body of water. Land use (*i.e*., urban, rural, forested, agricultural, and industrial) should be considered when locating sample sites, because man-made activities significantly affect the amount of sedimentation, nutrients, and organic or inorganic compounds entering a given segment of a river, lake, or stream. The location of permitted dischargers should be reviewed, using the database provided by the DWR's NPDES Unit. Discussion of the proposed study with regional office personnel can also provide additional information useful for determining sampling locations. Pre-study planning of this nature will enhance data interpretation once collections and analyses begin.

- **Methods** - Sampling techniques should be listed with reference to those described in this manual. Any deviation from these standard methods must be noted and described.

- **Analytical Requirements** - All water chemistry and quality parameters to be collected, and analyses that will be required, should be noted.

- **Logistics** - Shall include estimates of manpower requirements, equipment needed, time requirements, methods of sample transport to laboratories, *etc*. The study plan must be submitted and approved by the employee's supervisor prior to conducting the investigation.

A study is complete when a written memorandum is sent to and approved by the appropriate level of management (typically the Environmental Sciences Section Chief) within the DWR. Each memorandum should contain these sections: an **Introduction or Background**, **Sampling Sites**, **Methods**, **Results and Discussion,** and **Summary or Recommendations**. Any figures, maps, and photographs needed to allow a reader to easily locate the sampling sites should also be included. When the report or memorandum is approved, an Intensive Survey Branch file number is assigned. Finally, the report or memorandum is filed in a Projects File.

3.0 FISH TISSUE

Because fish spend their entire lives in the aquatic environment, they incorporate chemicals from this environment into their body tissues. Contamination of aquatic resources have been documented for heavy metals, pesticides, and other complex organic compounds. Once these contaminants reach surface waters, they may be available for bioaccumulation, either directly or through aquatic food webs, and may accumulate in fish and shellfish tissues. Results from fish tissue monitoring can serve as an important indicator of further contamination of sediments and surface water.

This procedure is used by the DWR to collect and process fish tissue samples to be analyzed for chemical contaminants. These procedures are based on established guidelines described in USEPA (2000). The procedure does not include procedures used by the DWR's Analytical Chemistry Laboratory.

3.1 Study Design

A detailed sampling plan should be developed by the primary researcher and approved by the Intensive Survey Branch supervisor prior to initiating any studies. At minimum, a study should involve a two tiered approach:

- Screening, or Tier I studies, should identify sites where commonly consumed fish species are contaminated with target analytes and may pose a risk to human health.

- Intensive, or Tier II, studies should characterize the magnitude and geographical extent of contamination in harvestable fish at sites identified in Tier I studies. Tier II studies should also be designed to verify results of Tier I screening studies.

Further information on study objectives and sampling design may be found in USEPA (2000).

3.2 Sample Collection

In most cases the DWR will employ electrofishing as the primary means of fish collection. Collections on lakes and non-wadeable streams are usually accomplished using a boat mounted electrofisher powered by a 2.5 watt or a 7.5 watt generator. Collections on wadeable streams are accomplished using back pack electrofishing techniques (refer to the Fish Community Assessment SOP for details on this method).

During fish tissue sampling, a measured distance is not sampled, rather sampling is conducted until the required number of fish are collected. All personnel involved should be familiar with standard electrofishing operational and safety procedures (Reynolds 1996).

In certain cases electrofishing may not be effective especially when targeting Ictalurids (catfishes) and other benthic species. In these cases, trot lines, traps, or gillnets may be used (Hubert 1996).

Certain studies may require that fish be collected by other agencies or that fish be purchased from commercial fishermen. DWR personnel should provide quality control measures necessary to ensure that samples are collected and handled properly with minimal contamination and that sampling sites are verified.

At each sampling station personnel should fill out a Fish Tissue Survey Form (Appendix B) to provide additional information regarding the site visit. The form allows field staff to document access conditions, all species observed during electrofishing, water quality measurements, disease information, and any comments about the station.

3.3 Sample Shipment and Handling

Fish collected for analyses must be shipped to the processing laboratory in such a manner as to prevent decomposition or contamination. Fish should be removed from live wells, holding tanks, or buckets, rinsed with ambient water to remove foreign matter, and placed on a contaminant free surface for sorting. Skins on fish selected for analysis should be examined for breaks or lacerations from sampling gear - a possible source of contamination. Fish samples should be sorted by species before packaging for shipment.

Fish selected for metals analysis are placed by species in polyethylene bags. After removing as much air as possible, the bags are sealed and tagged with the date, time, station name, species, and collector(s).

Fish selected only for organics analyses, including dioxins, are wrapped whole in clean aluminum foil with the dull side of the foil against the skin of the animal. Large spines on any fish should be sheared to minimize puncturing of the foil. Wrapped fish are sorted by species and placed in tagged polyethylene bags as described for metals samples.

Packaged fish are placed immediately on wet ice and chilled to 4°C for transport back to the laboratory. Samples shipped on wet ice should reach the processing laboratory within 24 hours of collection to allow sufficient time for processing. Samples to be filleted should be processed no later than 48 hours after collection.

If samples cannot be processed within this time frame then they should be frozen as whole fish, delivered to the laboratory as soon as possible, and stored at -20 ^{o}C until processing can be performed. **Freezing samples should be avoided whenever possible due to the possibility of rupturing internal organs and contaminating fillet tissue.** If fish are frozen they should not be allowed to thaw during transport. Prior to processing, frozen fish samples should only be partially thawed before filleting (ice crystals should still be visible in the fillet tissue).

3.4 Laboratory Procedures

All laboratory personnel performing sample processing procedures should be trained or supervised by an experienced biologist.

Individual fish received for filleting should be unwrapped and inspected carefully to ensure that they have not been compromised in any way (i.e., not properly preserved during shipment). Any specimen deemed unsuitable for further processing and analysis should be discarded and identified on the sample processing record.

A wet weight is determined for each fish to the nearest gram and recorded on the Fish Tissue Raw Datasheet (Appendix A). All samples should be weighed on balances that are properly calibrated and of adequate accuracy and precision to meet program data quality objectives. Balance calibration should be checked at the beginning of each weighing session.

A total length is determined for each fish to the nearest centimeter using a length board such as the Wildco® Model 118 and recorded on the Fish Tissue Raw Datasheet (Appendix A).

Individual fish are identified to species under the supervision of an experienced biologist familiar with North Carolina fish fauna. Fish are first identified using current, regional identification manuals and other appropriate taxonomic literature (ie:Menhinick, E. F. 1991). If questions occur, identifications are verified by other taxonomists in the Environmental Sciences Section or by personnel from the North Carolina Museum of Natural Science.

Processing Equipment: Equipment used in processing samples for metals analysis should be made of stainless steel, glass, or plastic. Chromium and nickel contamination can occur from the use of stainless steel. Therefore, if these metals are of concern, other materials should be used during sample processing. Equipment used in processing samples for organics analysis should be made of stainless steel, glass, or anodized aluminum.

Prior to preparing metals samples, all surfaces in the processing laboratory are washed with a detergent and rinsed with a metal free water (treated by reverse osmosis). Utensils and containers should be cleaned thoroughly with a detergent solution, rinsed with tap water, soaked in 50 percent HNO3 , for 12 to 24 hours at room temperature, and then rinsed with organics- and metal-free water. Note: Chromic acid should not be used for cleaning any materials. Acids used should be at least reagent grade. Stainless steel parts may be cleaned using this recommended procedure with the acid soaking step method omitted (Stober, 1991).

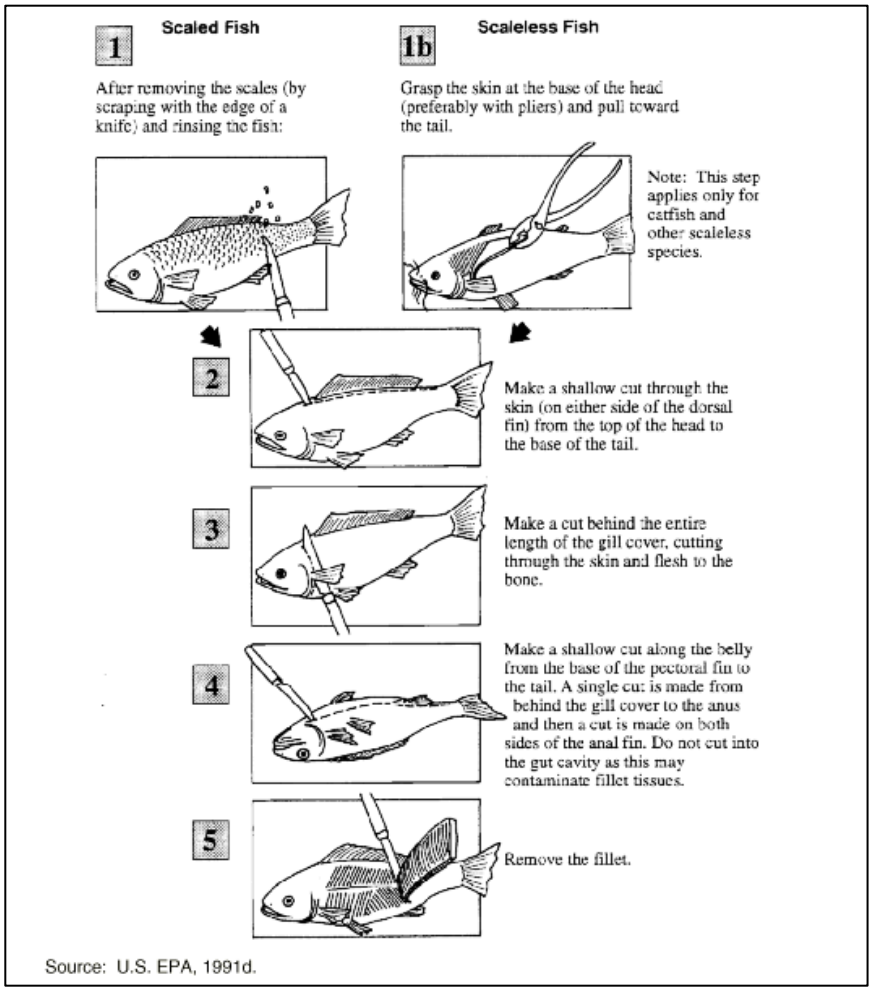
Equipment used in processing samples for organics analysis should be of stainless steel, anodized aluminum, borosilicate glass, polytetrafluoroethylene (PTFE), ceramic, or quartz. Polypropylene and polyethylene (plastic) surfaces, implements, gloves, and containers are a potential source of contamination by organics and should not be used. If a laboratory chooses to use these materials, there should be clear documentation that they are not a source of contamination. Filleting should be done on glass or PTFE cutting boards that are cleaned properly between fish or on cutting boards covered with heavy duty aluminum foil that is changed after each filleting. Tissue should be removed with clean, high-quality, corrosion-resistant stainless steel or quartz instruments or with knives with titanium blades and PTFE handles (Lowenstein and Young, 1986). Fillets or tissue homogenates may be stored in borosilicate glass, quartz, or PTFE containers with PTFE-lined lids or in heavy duty aluminum foil (see Table 7-1). Prior to preparing each composite sample, utensils and containers should be washed with detergent solution, rinsed with tap water, soaked in pesticide-grade isopropanol or acetone, and rinsed with organic-free, distilled, deionized water. Work surfaces should be cleaned with pesticide-grade isopropanol or acetone, washed with distilled water, and allowed to dry completely. Knives, fish scalers, measurement boards, etc., should be cleaned with pesticide-grade isopropanol or acetone followed by a rinse with contaminant-free distilled water between each fish sample (Stober, 1991). The total length of each fish is determined to the nearest millimeter and the wet weight of each fish is determined to the nearest gram. Fish are weighed on foil lined trays and the foil is changed between each species. All data are recorded on the laboratory data sheet (Appendix A).

Scaling: Scaling is performed on cleaned stainless steel or plastic surfaces covered in heavy duty aluminum foil. Separate cutting boards and utensils are used for scaling and skinning to prevent cross contamination of tissues. Fish are scaled prior to filleting using an automatic rotary scaler and rinsed with water filtered *via* reverse osmosis (R.O.) to remove slime and foreign matter. The scaling surfaces are also rinsed between fish to prevent contamination. Scaleless fish (catfish) are skinned prior to filleting.

Fillets: Filleting is performed on plastic or stainless steel surfaces covered with heavy duty aluminum foil. Aluminum foil is rinsed with R.O. water between fish from the same station and changed completely between stations. Filleting is performed using cleaned bare hands or talc free disposable gloves. Hands or gloves should be rinsed between samples to prevent cross contamination. Fillets are ressected using high grade stainless steel knives cleaned according to the above directions. Knives are rinsed with R.O. water between fish from the same station and recleaned or changed between stations.

Fillets should be ressected according to the general procedure (Figure 1). Fillets should be removed from the lateral area of the fish behind the head and pectoral fin and should include the belly flap. **Care should be taken not to cut into the gut cavity as it may contaminate the fillet tissue.**

Figure 1. Procedure for filleting fish.



Source: U.S. EPA, 1991d.

Fillets are ground and homogenized prior to analysis to ensure equal distribution of contaminants throughout the sample. Fillets are ground using a glass and stainless steel high speed blender or Hobart® Model 8145 commercial grinder. Samples are ground until they appear homogenous. Samples processed in the Hobart® Model 8145 commercial grinder are removed from the grinder and further mixed by hand. Hand mixing is accomplished by dividing the sample into quarters, mixing opposite quarters, and then mixing the remaining halves. Composite samples are prepared from at least 4 but no more than 10 individuals of the same species and should be of the same general size class. **Individuals of different species are never mixed to form composite samples.**

Final Sample: The final individual or composite samples should be composed of at least 100 g of tissue to ensure an adequate amount of material for analysis. Metals samples are placed in foil cups with foil lined lids, and labeled. Organics samples are wrapped in aluminum foil, dull side against the tissue, then wrapped in plastic to prevent desiccation.

All samples are then sent either directly to the DWR's Analytical Chemistry Laboratory (or other analytical laboratory), or frozen immediately and stored at -20 °C for later analysis.

3.5 Quality Assurance/Quality Control

To assess total variability, duplicate samples will be prepared from at least 10% of the fish samples. Duplicates are prepared using tissue from the same fillet or composite homogenate. Duplicates are assigned a "dummy" sample identification which is recorded in the processing laboratory log. The analytical laboratory does not receive this information.

During intensive or Tier 2 studies, portions of at least 10% of the prepared homogenates will be frozen at -20 ^{o}C and archived at the DWR's Water Quality Laboratory for a period of at least 6 months after completion of the study. This is done in case of analytical problems or the need for future references.

To assess interlaboratory variability, the DWR will attempt to split sample homogenates with other laboratories for analysis at least twice per year. Numbers of splits will depend on time and resource constraints of participating laboratories. Results from splits are tallied and plotted using descriptive statistics. Laboratory variability is considered acceptable if it is within two standard deviations of the mean for all measurements.

3.6 Data Analysis and Reporting

Data reported from the analytical laboratory below the method quantitation limit (MQL) are assigned a value of one-half the MQL. Data reported at or above the MQL are used as reported. The following statistics are calculated for each sampled species at each site:

- Range of target analyte concentrations;
- Arithmetic mean of target analytes;
- Standard deviation of mean target analyte concentrations; and
- Number of samples

Comparisons are performed using the Student t-Test (parametric) or the Sign Test (nonparametric).

In evaluating fish tissue analysis results, several criteria are used. Human health concerns related to fish consumption are screened by comparing results with federal Food and Drug Administration (FDA) action levels (USFDA 1980), Environmental Protection Agency (EPA) recommended screening values, and criteria adopted by the state Health Director (Table 1). Results which seem to be of potential human health concern are evaluated by the N.C. Division of Occupational and Environmental Epidemiology by request from the DWR.

The FDA levels were developed to protect people from the chronic effects of toxic substances consumed in foodstuffs and thus employ a "safe level" approach to fish consumption. Presently, the FDA has developed metals criteria only for mercury.

The EPA has recommended screening values for target analytes formulated from a risk assessment procedure (USEPA 2000). These are the concentrations of analytes in edible fish tissue that are of potential public health concern. The DWR compares fish tissue results with EPA screening values to evaluate the need for further intensive site specific monitoring.

The North Carolina State Health Director has adopted a selenium limit of 10 µg/g for issuing an advisory. Although the USEPA has suggested a recreational fishers screening value of 0.26 ppt (pg/g) for dioxins, the State of North Carolina currently uses a value of 4.0 ppt in issuing an advisory.

Table 1. Fish tissue criteria.

All wet weight concentrations are reported in parts per million (ppm, µg/g), except for dioxin which is in parts per trillion (ppt, pg/g).

Contaminant	FDA Action Levels	US EPA Screening Values Recreational Fishermen	US EPA Screening Values Subsistence Fishermen	NC Health Director
Metals				
Arsenic (Inorganic)		1.2	0.00327	
Cadmium		4.0	0.491	
Mercury	1.0	0.3	0.049	0.4
Selenium		20	2.457	10.0
Tributyltin		1.2	0.147	
Organics				
Aldrin	0.3			
Chlorpyrifos		1.2	0.147	
Total chlordane		0.114	0.014	
Cis-chlordane	0.3			
Trans-chlordane	0.3			
Total DDT[1]		0.117	0.0144	
o, p DDD	5.0			
p, p DDD	5.0			
o, p DDE	5.0			
p, p DDE	5.0			
o, p DDT	5.0			
p, p DDT	5.0			
Diazinon		2.8	0.344	
Dicofol		1.6	0.196	
Dieldrin		0.0025	3.07×10^{-4}	
Dioxins (total)		2.56×10^{-7}	3.15×10^{-8}	4.0 (ppt)
Disulfoton		0.16	0.019	
Endosulfan (I and II)		24	2.949	
Endrin	0.3	1.2	0.147	
Ethion		2.0	0.245	
Heptachlorepoxide		0.00439	5.40×10^{-4}	
Hexachlorobenzene		0.025	0.00307	
Lindane		0.0307	0.00378	
Mirex		0.8	0.098	
Oxyfluorfen		0.546	0.0671	
Total PCBs		0.02	0.00245	0.05
PCB-1254	2.0			
Terbufos		0.08	0.009	
Toxaphene		0.0363	0.00446	

[1] Total DDT includes the sum of all its isomers and metabolites (i.e. p, p DDT, o, p DDT, DDE, and DDD).

[2] Total chlordane includes the sum of cis-and trans- isomers as well as nonachlor and oxychlordane.

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USEPA. 2000. Guidance for assessing chemical contaminant data for use in fish advisories. Vol. 1: Fish sampling and analysis. 3rd Edition. Washington, DC. Office of Water. EPA 823-B-00-007.

USFDA. 1980. Action levels for poisonous or deleterious substances in human food and animal feed. Shellfish Sanitation Branch, Washington, DC.

SOP Appendix A. Fish tissue raw data sheet.

Station **County** **Subbasin** **8 Digit HUC** _____

Latitude _____ **Longitude** _____ **Collection Date** _____

Processing Date _____ **Date To Lab** _____

Station Comments _____

Species Code	Total Length (mm)	Weight (g)	DWR Number	Comments

Fish Tissue Survey Information

Waterbody: _____**Location:** _____**Study Site #:** _____

Latitude: _____**Longitude:** _____**Nearest City/Town/Landmark:** _____

County: _____**Subbasin:** _____**8 digit HUC:** _____

Survey Date/Time: _____**Survey Duration: Hours:**_____ **Min:** _____

Staff: _____

Survey Method: Big Boat ☐ Small Boat ☐ Back Pack ☐ Other ☐ Describe:_____

Ramp Info: Wildlife ☐ Marina ☐ Public ☐ Private ☐ Other ☐ Describe:_____

Ramp Condition: Paved ☐ Sand ☐ Gravel ☐ Earth ☐ Slide in ☐ Comments:_____

Water Quality Measurements: Temp: _____ **pH:** _____ **D.O.:** _____ **Cond:** _____**Salinity:** _____

Species Observed:

__ AMERICAN EEL
__ BLACK BULLHEAD
__ BLACK CRAPPIE
__ BLUEGILL SUNFISH
__ BLUE CATFISH
__ BLUEHEAD CHUB
__ BOWFIN
__ BROOK TROUT
__ BROWN BULLHEAD
__ BROWN TROUT
__ CARP
__ CHAIN PICKEREL
__ CHANNEL CATFISH
__ CREEK CHUBSUCKER
__ FLAT BULLHEAD
__ FLATHEAD CATFISH
__ FLIER
__ GIZZARD SHAD
__ GOLDEN SHINER
__ GREEN SUNFISH
__ LARGEMOUTH BASS
__ LONGNOSE GAR
__ NORTHERN HOGSUCKER
__ PINFISH
__ PUMPKINSEED
__ QUILLBACK
__ RAINBOW TROUT

__ REDBREAST SUNFISH
__ REDEAR SUNFISH
__ REDFIN PICKEREL
__ REDHORSE SUCKER
__ GOLDEN REDHORSE
__ NOTCHLIP REDHORSE
__ SHORTHEAD REDHORSE
__ ROCK BASS
__ SMALLMOUTH BASS
__ SMALLMOUTH BUFFALO
__ SNAIL BULLHEAD
__ SPOTTED BASS
__ SPOTTED SUCKER
__ SPOTTED SUNFISH
__ STRIPED BASS
__ STRIPED KILLIFISH
__ STRIPED MULLET
__ WALLEYE
__ WARMOUTH
__ WHITE BASS
__ WHITE CATFISH
__ WHITE CRAPPIE
__ WHITE PERCH
__ WHITE SUCKER
__ YELLOW BULLHEAD
__ YELLOW PERCH

OTHER SPECIES:

Disease Observed: Lesions/Sores ☐ Injuries ☐ Flared Gills ☐ Excessive Mucus ☐ Tumors ☐ Visible Parasites ☐
Other ☐ Describe:_____

Species Collected:

Station Comments/Notes:

APPENDIX 2:

ROUTINE FISH TISSUE ANALYTES

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Appendix 2: Routine FTMP Fish Tissue Analytes

Metals	Pesticides	Congener #	PCBs	PCB Aroclors
Arsenic	Aldrin	1	Chlorobiphenyl	1016
Cadmium	BHC-Alpha	5	Dichlorobiphenyl	1221
Chromium	BHC-Beta	18	Trichlorobiphenyl	1232
Copper	BHC-Gamma	31	Trichlorobiphenyl	1242
Mercury	BHC-Delta	44	Tetrachlorobiphenyl	1248
Lead	Chlordane, Technical	52	Tetrachlorobiphenyl	1254
Nickel	Chlordane-Alpha	66	Tetrachlorobiphenyl	1260
Selenium	Chlordane-Gamma	87	Pentachlorobiphenyl	1262
Zinc	Trans-Nonachlor	101	Pentachlorobiphenyl	
	Chlorpyrifos	110	Pentachlorobiphenyl	
	DDD, 2,4'	138	Hexachlorobiphenyl	
	DDD, 4,4'	141	Hexachlorobiphenyl	
	DDE, 2,4'	151	Hexachlorobiphenyl	
	DDE, 4,4'	153	Hexachlorobiphenyl	
	DDT, 2,4'	170	Heptachlorobiphenyl	
	DDT, 4,4'	180	Heptachlorobiphenyl	
	Dieldrin	183	Heptachlorobiphenyl	
	Endosulfan I	187	Heptachlorobiphenyl	
	Endosulfan II	206	Nonachlorobiphenyl	
	Endosulfan Sulfate			
	Endrin			
	Endrin Aldehyde	**Congener #**	**PBDE**	
	Endrin Ketone	47	Tetrabromodiphenyl Ether	
	Heptachlor	99	Pentabromodiphenyl Ether	
	Heptachlor Epoxide	153	Hexabromodiphenyl Ether	
	Hexachlorobenzene			
	Methoxychlor			
	Mirex			
	Pentachloranisole			

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APPENDIX 3:

Quality Assurance Manual for the NC Division of Water Resources Laboratory Section

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

April 2004

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

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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 DWQ.

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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. The Division of Water Quality (DWQ) Laboratory Section is committed to protecting North Carolina's environment and human health by providing the highest quality data obtainable with reasonable cost and effort and the best overall service in environmental testing. The Laboratory 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 DWQ 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 Laboratory 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 Laboratory 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 Laboratory 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 analysts 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.**

Following is a list of documents used to develop the Laboratory Section's QAMP.

- Interim Draft EPA Requirements for Quality Management Plans, U.S. Environmental Protection Agency, EPA QA/R-2, July 1993 et seq.
- EPA Requirements for Quality Assurance Project Plans, EPA 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.
- International Standard ISO/IEC Guide 17025 - 1999 et seq.
- NELAC standards, Chapter 5, Quality Systems
- The North Carolina Administrative Code, 15A NCAC 2H .0800, governing Laboratory Certification.

3.1 Analytical Laboratory Services

The DWQ Laboratory Section 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 stream, wastewater, groundwater, soil, sediment and fish tissue samples.
- Provides consultation and assistance to Divisional personnel, 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 Quality's Laboratory Section provides chemical, physical and microbiological analyses of surface water, groundwater, sediment, fish tissue and spill samples from around the state for the Division's Water Quality and Groundwater Sections and the Underground Storage Tank Section of the Division of Waste Management. The Quality Assurance/Quality Control (QA/QC) Coordinator 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 Quality Laboratory Section. The QA/QC Coordinator 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 Laboratory 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 Quality, NC Division of Solid Waste Management, NC Division of Marine Fisheries, Dept. of Health and Human Services, municipal governments, USEPA, and US Centers for Disease Control.

3.2 Ethics

All employees of the DWQ Laboratory 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' (see 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 DWQ Laboratory 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 lab 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 enhancing.

- **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 leaving less than the minimum number of calibration points required by a method 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 and/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 DWQ Laboratory 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.

Figure 3-1. Code of Ethics Statement Form

NC DWQ
Laboratory 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 DWQ Laboratory 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 lab 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 enhancing.
- **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 leaving less than the minimum number of calibration points required by a method 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.

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 DWQ Laboratory 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

4.0 Organization, Facilities and Equipment

The Laboratory Section is a section of the Division of Water Quality of the North Carolina Department of Environment and Natural Resources. The Laboratory Section is comprised of managers, chemists, technicians, and support personnel. The main laboratory (referred to as the *Central Laboratory*) is located in Raleigh, NC. Two satellite laboratories are strategically located in the eastern (Washington, NC) and western (Swannanoa, NC) regions of the state to provide assistance with time-sensitive tests. These are referred to as the *WARO Laboratory* and the *ARO Laboratory*, respectively.

The Central Laboratory is divided into two analytical branches: the Organic Chemistry Branch and the Microbiology & Inorganic Chemistry Branch. The Organic Chemistry Branch is subdivided into two analytical units: Volatile Organics and Semivolatile Organics/Pesticides. The Microbiology & Inorganic Chemistry Branch is subdivided into three sections: Bio/Chemistry Unit, Metals Unit and Regional Labs. The Bio/Chemistry Unit is further subdivided into three analytical units: Wet Chemistry, Nutrients and Microbiology. There is also a Support Branch, which provides assistance to all of the sections listed above. The Laboratory Certification Branch is responsible for certifying commercial, industrial, municipal and field laboratories engaged in wastewater analyses and monitoring for North Carolina facilities.

The Laboratory Section 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 Branch Managers. A Supervisor is assigned to each analytical unit to oversee the daily operations of these units. The QA/QC Coordinator has the responsibility of establishing, implementing and coordinating all activities related to the quality assurance program. The QA/QC Coordinator manages the QA/QC program for the three laboratories, including working with lab management and staff to identify improvements to QA systems, and establishing policy for the Laboratory 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.

An organization chart of the Laboratory Section is provided in Figure 4-1.

4.1 Responsibilities of Key Positions

4.1.1 Section Chief (ESIV)

Directs the activities of the Laboratory Section. Responsibilities include providing direction to the various laboratory branches and units including laboratory operations, accounting, procurement, QA/QC, and customer service. General duties involve budgeting, decisions on equipment, development of policies, personnel issues, working with clients on various matters and signatory authority for all Certification actions. The Section Chief authorizes any significant changes to the Quality Assurance Manual, in writing.

4.1.2 Quality Assurance/Quality Control Coordinator (CIII)

Plans, implements and assesses the Laboratory Section QA program. Manages the laboratory's blind proficiency program. The QA/QC Coordinator 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. The employee distributes controlled copies of the QAM to all affected personnel and provides training in its interpretation. The employee ensures all routinely used procedures that impact data quality are documented in standard operating procedures (SOP's) that are complete and have been reviewed and approved by both management and the staff responsible for implementing those procedures. The employee coordinates audits/reviews to assure adherence to the QAM and to identify deficiencies in the QA/QC systems. The employee subsequently makes appropriate recommendations for correction and improvement of QA/QC activities by means of written reports. The QA/QC Coordinator ensures adequate follow-through actions are implemented in response to audit/review findings. The QA/QC Coordinator also coordinates external audits and serves as the primary liaison with regulatory agencies to ensure the labs' compliance with all pertinent regulatory and accreditation requirements.

4.1.3 Organic Chemistry Branch Manager (CSIV)

Supervises the Volatile Organics and Semivolatile Organics/ Pesticides analytical units of the Central Laboratory. 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 Supervisors 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 Unit Supervisors.

4.1.4 Microbiology and Inorganic Chemistry Branch Manager (CSIV)

Supervises the Bio/Chemistry section and Metals analytical unit of the Central Laboratory and the Regional laboratories. 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 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 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. Certifies analytical reports for release to clients. Performs work performance reviews of Unit Supervisors and Regional Office personnel.

4.1.5 Bio/Chemistry Unit Supervisor (CSII)

Oversees the daily operation of the Wet Chemistry, Nutrients, and Microbiology analytical units of the Bio/Chemistry Unit. Responsible for training of staff, monitoring daily work plans 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; supervising analysts and 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. Provides significant amount of customer support and consulting. Performs work performance reviews of unit personnel.

4.1.6 Metals Unit Supervisor (CIII)

Oversees the daily operation of the Metals 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; supervising analysts and 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. Provides significant amount of customer support and consulting. Performs work performance reviews of unit personnel.

4.1.7 Volatiles Unit Supervisor (CIII)

Oversees the daily operation of the Volatile Organic 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; supervising analysts and 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. Provides significant amount of customer support and consulting. Performs work performance reviews of unit personnel.

4.1.8 Semivolatile Organic/Pesticides Unit Supervisor (CIII)

Oversees the daily operation of the Semivolatile Organic/Pesticides Unit, which is responsible for the analysis of semivolatile organics, pesticides and acid herbicides by GC and GC/MS techniques. 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; supervising analysts and 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. Provides significant amount of customer support and consulting. Performs work performance reviews of unit personnel.

4.1.9 Chemists/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 SOP's 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 Branch Manager 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 SOP's, such as organic extractions, metals digestion, or wet chemistry. 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. Conduct sample receiving procedures including unloading coolers, organizing samples, comparing samples to chain-of-custody documentation, taking sample temperatures, and labeling samples. Perform routine tasks such as shipping, bottle preparation, acting as liaison with the state and private courier services, and performing sample disposal. Reference materials regarding hold times, containers, and preservatives. Prepare receipt non-conformance reports and manage sample distribution. Responsibilities may also include (but are not limited to) glassware cleaning. Report to the Section Chief. Perform additional tasks as requested. Comply with all policies in the QA manual and Chemical Hygiene Plan.

4.1.11 Processing Assistant (PAIII)

Enters sample information into the computerized DWQ Sample Tracking and Reporting (DWQ STAR) system. Verifies and notifies Unit Supervisors of samples that have not been reported within target turnaround times. Generates final reports and after they have been checked for completeness, sends them to the appropriate client.

4.1.12 Processing Assistant (PAIV)

Serves as primary receptionist for the Central Chemistry lab. Checks data entry into DWQ STAR and reviews final reports for completeness. Serves as backup to Processing Assistant III position. Manages data filing and data archiving for the Laboratory Section. Receives and distributes correspondence by mail or facsimile. Provides secretarial assistance to the Laboratory Section in the form of typing forms, records, correspondence, memoranda, reports, minutes of meetings, scientific or technical material and numerical data from rough draft or corrected copy. Oversees maintenance on office equipment.

4.2 Personnel Orientation and Training

All activities performed by the Laboratory Section shall be accomplished by qualified personnel. Each individual engaged in the conduct of, or responsible for the supervision of, sample handling and analysis shall have education, training, and experience, or a combination thereof, to enable that individual to perform the assigned

functions. Each operating unit shall have job descriptions for all positions. These job descriptions shall 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 exceeding satisfactory.

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*. 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

Each new employee will take part in a two-tiered safety orientation process that will include a Division orientation with the Division Safety Officer and a Laboratory Section orientation with the employee's Supervisor. The Division safety orientation will include Hazard Communication and Chemical Hygiene Plan (CHP) review consistent with the requirements 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 process is documented on the *CHP Orientation Training* form (see Figure 4-2) and filed in the employee's Training Documentation File and the Division Training files.

The Laboratory Section safety orientation is an in-depth examination of the Laboratory Section's Chemical Hygiene Plan. On employment with the Laboratory Section, new personnel will receive a copy of the Chemical Hygiene Plan. The employee is required to sign a statement (see *Certification of Unit Training* form in Figure 4-3) indicating that orientation information was made available, that they have viewed the CHP, and understand the information contained in that document. The Unit Supervisor will allow adequate time, before beginning work, to read the document and clarify any areas that are not understood. This general safety orientation 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.
- Personal protective equipment.

4.2.1.3 Supervisory Orientation

During the supervisory orientation, the new employee's Branch Manager or Unit Supervisor provides the employee with a basic understanding of the role of the laboratory within the Division of Water Quality and the basic elements of that individual's position within the laboratory. Personnel issues such as timesheets, workplans and the application process are reviewed. The employee is required to sign a statement (see *Employee Orientation Checklist* in Figure 4-4) indicating that the checked items were discussed and that the employee understands and agrees to abide by those policies and procedures.

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. Unit Supervisors will be responsible for unit-specific chemical hygiene training for new employees. All unit safety training is documented on a *New Employee Safety Orientation and Training* form (see Figure 4-5). A copy is kept in the employee's Training Documentation File and a copy forwarded to the Division Safety Officer for inclusion in the Division 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 Material Safety Data Sheet (MSDS) 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.

Any time substantial changes are made to the CHP, all Laboratory Section employees will receive update 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.

Unit 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/technician is capable of performing either independently or only with supervision. The file shall include, at a minimum, the following:

- Job description
- Performance Management Work Plan

- Resume
- Code of Ethics Statement form
- Orientation forms
- Certificates of coursework completion
- Training forms and associated IDOCs and MDLs
- Performance testing results
- Audit reports and corrective action responses
- Emergency contact information

The Unit Supervisor is responsible for keeping a Training Documentation File for each person under his or her supervision that is up-to-date and current.

New laboratory personnel are trained in basic lab techniques, safety and chemical hygiene, chemistry theory of the test procedures employed, quality control procedures, the DWQ STAR LIMS, record keeping and the operating principles and regulations governing the methods employed by the Laboratory Section. A designated chemist/technician and/or the Unit Supervisor closely supervise every new employee until he/she exhibits proficiency in accepted laboratory techniques. This process includes reading specific SOP's and other associated references. Once a chemist/technician demonstrates a technological aptitude within the framework of the Quality Assurance program, he/she will perform an Initial Demonstration of Capability (IDOC) study and a Method Detection Limit study (MDL), if applicable. This training process is documented (see SOP/Method Training Summary form - Figure 4-6, IDOC form - Figure 4-7, and MDL form - Figure 4-8) 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 or Branch Manager should 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 (as necessary) all Standard Operating Procedures (SOPs) annually that pertain to the work they perform within the laboratory. Any updates to SOPs must have the approval of the Supervisor, Branch Manager and QA Coordinator and must conform to the policies of the laboratory. It is the responsibility of the Supervisor to ensure that documentation demonstrating that their employees have read, understand and are using the latest version of SOPs is current and on file. The latest official versions of SOPs are only located on the Laboratory Section Intranet site (http://www.esb.enr.state.nc.us/lab/qa/sop.htm) and are accessible to all analysts and technicians throughout the Laboratory Section.

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. 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 or Branch Manager, an analyst may demonstrate proficiency in a test method without going through the formal training process. A *Statement of Capability* form (Figure 4-9) 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, participation in training workshops, acceptable PT results, or an IDOC study. The completed form will be maintained in the analyst's Training Documentation File.

4.3 Facilities

The Central Laboratory building 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 Facility Management Division 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 4-10.

The Asheville Region Laboratory is housed in the Asheville Regional Office in Swannanoa, NC. 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 4-11.

The Washington Region Laboratory is housed in the Washington Regional Office in Washington, NC. The total laboratory area consists of approximately 1225 square feet with approximately 79 linear feet of bench space. This consists of a main laboratory and office space. A floorplan of the WARO Laboratory is presented in Figure 4-12.

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 Laboratory 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 building is always locked and keys are distributed to all permanent employees. The main

entrance and the Receiving Room (G-098) doors are equipped with an electric lock that can be released by lab personnel. Under special circumstances, sample storage coolers may be locked as well and assigned custodians will control access to each.

The regional laboratories shall store Chain-of-Custody samples in secure or locked areas.

4.4 Equipment

4.4.1 Inventory

The laboratories are equipped with a diversity of 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 and/or calibrations concerned. Instrument serial numbers or assigned ID numbers are recorded on all 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. The major equipment housed in each laboratory is detailed in Tables 4-1: Central Laboratory, 4-2: Asheville Regional Laboratory and 4-3: Washington Regional Laboratory.

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 cooling fan operation, pump operation, indicator readings, mechanical checks, clean air filters, clean tubing, clean cells, etc.
- Routine preventive maintenance on all major equipment is performed as needed;
- 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/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, the Supervisor or Branch Manager steps in to help prior to calling the manufacturer's service representative.

Some 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 FIA systems and spare columns for 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

Where feasible, redundant equipment and instruments are maintained. In case one instrument goes down, another instrument can be used (e.g., 2 gas chromatographs or a backup dissolved oxygen meter) to meet hold times and/or client due dates. In some cases, samples may be routed to one of the other three labs of the Laboratory Section if they have the capability and if the samples will meet the published hold times.

Figure 4-1. North Carolina Division of Water Quality Laboratory Section Organization Chart

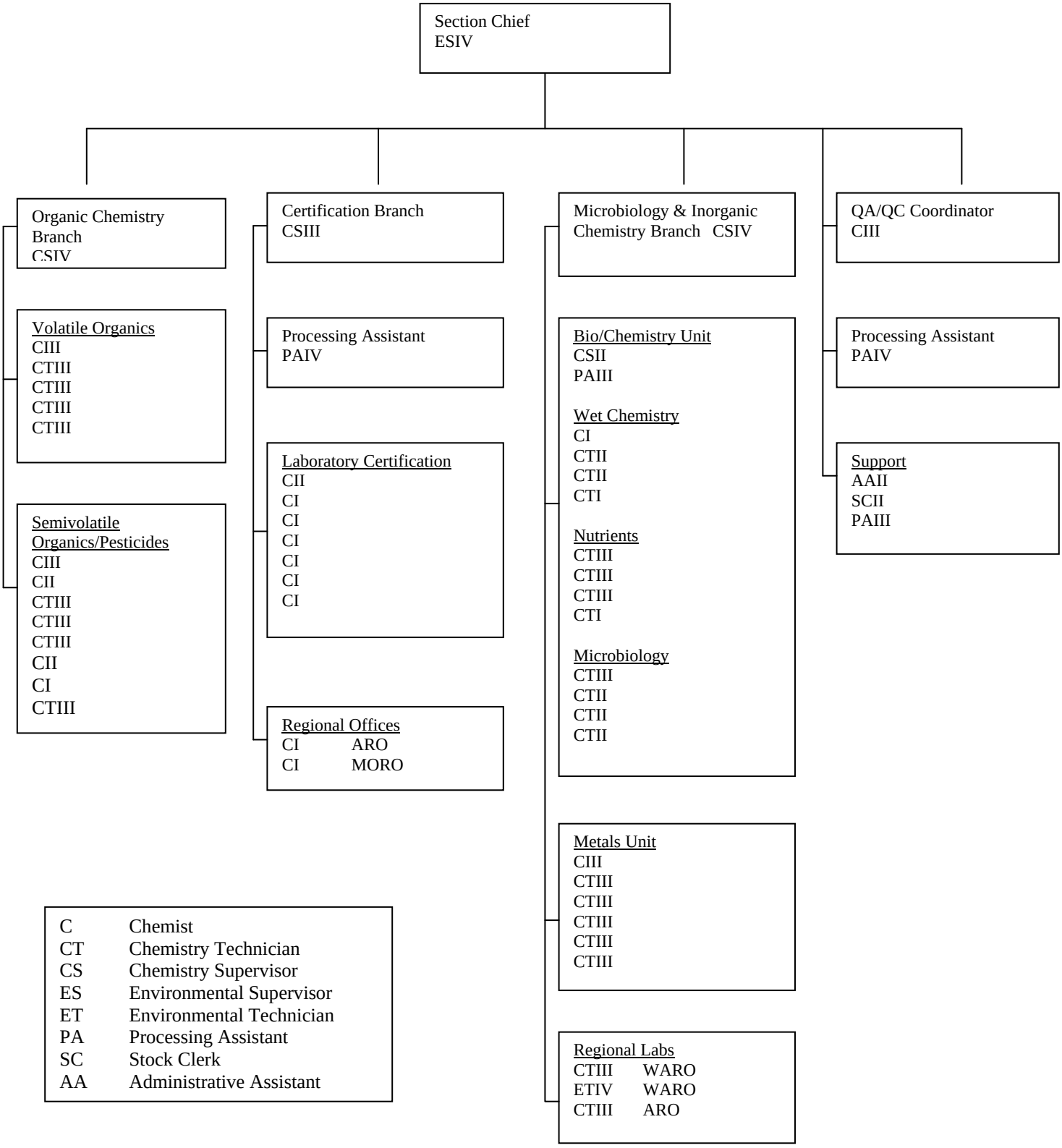


Figure 4-2. CHP Orientation Training Form

CHP Orientation Training

Date of Training:	
Name of Employee:	
Trainers (and initials):	Steve Kaasa

☐ **Hazard Communication Review (29 CFR 1910.1200)**
Hazard Classes of Chemicals used in the Laboraotry
Material 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

Figure 4-3. Certification of Unit Training Form

Certification of Unit Training

By my signature below, I acknowledge that I

was instructed by the below named individual on the hazards

present in _____ and the proper
location of areas (e.g., room number)

laboratory procedures to follow when working there as outlined

in the Chemical Hygiene Plan and any other operational plans for my work area.

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

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

_____ _____
Employee Signature Date

_____ _____
Supervisor Signature Date

Figure 4-4. Employee Orientation Checklist

Employee Orientation Checklist

During the supervisory orientation, the employee is provided with a basic understanding of the elements of that individual's position within the laboratory, and is familiarized with the work area and general policies and procedures.

- ☐ Job description (review within 30 days of hire)
- ☐ Performance Management Work Plan
- ☐ Work Schedule
- ☐ Rules regarding lunch and break period
- ☐ Timesheets (for a detailed explanation, consult Kimberly Moses at 733-7015 ext. 212)
- ☐ Absences/Tardiness/Leave/Compensatory Time/Adverse Weather
- ☐ Telephone Operation
- ☐ Use of State Property (e.g., internet, telephone, computer, fax, copier, vehicle use, etc.)
- ☐ Mail Procedures
- ☐ Location and storage of personal belongings
- ☐ Travel Procedures (for detailed explanation, consult Tony Bass, DWQ Budget at 733-7015 ext. 220)
- ☐ Organization Chart
- ☐ Access to Policy Manuals (internet links are provided in New Employee Notebook)
- ☐ Impact of job/work on the Department, the public and co-workers
- ☐ Work Area
- ☐ Location of restrooms, break rooms and smoking areas
- ☐ Pay day/direct deposit
- ☐ Employee Health programs
- ☐ Drug and alcohol abuse policy and programs
- ☐ Employee suggestions/open door policy
- ☐ Parking/building security
- ☐ Tour of the laboratory and facilities/introduction to co-workers and key personnel
- ☐ Obtain key to building/work area
- ☐ Obtain personal protective equipment (e.g., labcoat, safety glasses/goggles/prescription, etc.)
- ☐ Schedule baseline physical (contact Mary Wiggins at Duke 8-919-286-5569, contract #EW03028)

By signing, the employee verifies that he/she has received, read and understands the information checked above.

Supervisor signature	Date
Employee signature	Date

Figure 4-5. New Employee Safety Orientation and Training Form

New Employee Safety Orientation and Training

Date of Orientation:	
Name of Employee:	
Orientation Instructor:	

Safety Plan Review

- ☐ Emergency Actions and Notification
- ☐ Reporting Laboratory Accidents
- ☐ Fire Prevention Guidelines
- ☐ Housekeeping Rules, Clothing and Personal Items
- ☐ Recognizing work area hazards

Personal Protective Equipment

- ☐ Location
- ☐ Instructions for Use (including cleaning, repairing and replacing)

Evacuation Plan

- ☐ When/where to Evacuate
- ☐ Alarm System (including tests and fire drills)

General Laboratory Hazards

- ☐ Hazardous Equipment
- ☐ Non-hazardous Equipment
- ☐ Electrical Hazards
- ☐ Compressed Gases
- ☐ Vacuums
- ☐ Noise Exposure
- ☐ Fume Hood Use
  - ☐ When one should use the Fume Hood
  - ☐ Operation of the Fume Hood

Chemicals used in the Laboratory

- ☐ Inventory of Chemicals used in the Laboratory
- ☐ Hazard Classes of Chemicals used in the Laboratory
  - ☐ Material Safety Data Sheets
  - ☐ Storage
  - ☐ Extremely Hazardous and Toxic Materials
- ☐ Transporting Chemicals
- ☐ Hazardous Waste Disposal
- ☐ _____
- ☐ _____

By signing, the employee verifies that he/she has received, read and understands the information checked above.

_____	_____	_____	_____
Signature of Employee	Date	Signature of Instructor	Date

Figure 4-6. SOP/Method Training Summary Form

SOP/METHOD TRAINING SUMMARY

Analytical unit/region		Instrument(s)	
Trainee		Technique	
SOP(s) reviewed		Date of completion	
Reference method(s)		Matrix	
Parameter			

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 preparation, etc.)
- ☐ QC Requirements (MS/MSD, QCS, blanks, duplicates, surrogates, internal standards, 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 ratios, etc.)
- ☐ Data Entry (DWQ STAR LIMS)
- ☐ Significant Figures
- ☐ Reporting Dilutions
- ☐ Reporting Data with Qualifier Codes

IV. GENERAL TRAINING

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

_____

_____

_____

_____

_____

V. RESULTS OF START-UP QC

IDOC Results	Acceptable:	Y / N / NA	Attach a copy of the IDOC study summary.
MDL Study (when applicable)	Completed:	Y / N / NA	Attach a copy of the MDL study summary.

VI. 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:	
Branch Manager Signature		Date:	
QA/QC Coordinator Signature:		Date:	

Figure 4-7. IDOC Summary Form

Initial Demonstration of Capability (IDOC) Certification Statement

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

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

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	Signature	Date
Branch Manager's Name	Signature	Date
Supervisor's Name	Signature	Date
Quality Assurance Officer's Name	Signature	Date

Figure 4-8. MDL Summary Form

Method Detection Limit (MDL) Study

Laboratory Name:		**Analytical Method:**	
Analyst(s) Name(s):		**SOP#:**	
Date:		**Instrument:**	
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 Deviation s	MDL	PQL

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 C.
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 4-9. 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 4-10. Central Laboratory Floorplan.

Central Laboratory
4405 Reedy Creek Road
Raleigh, NC 27607

(not to scale)

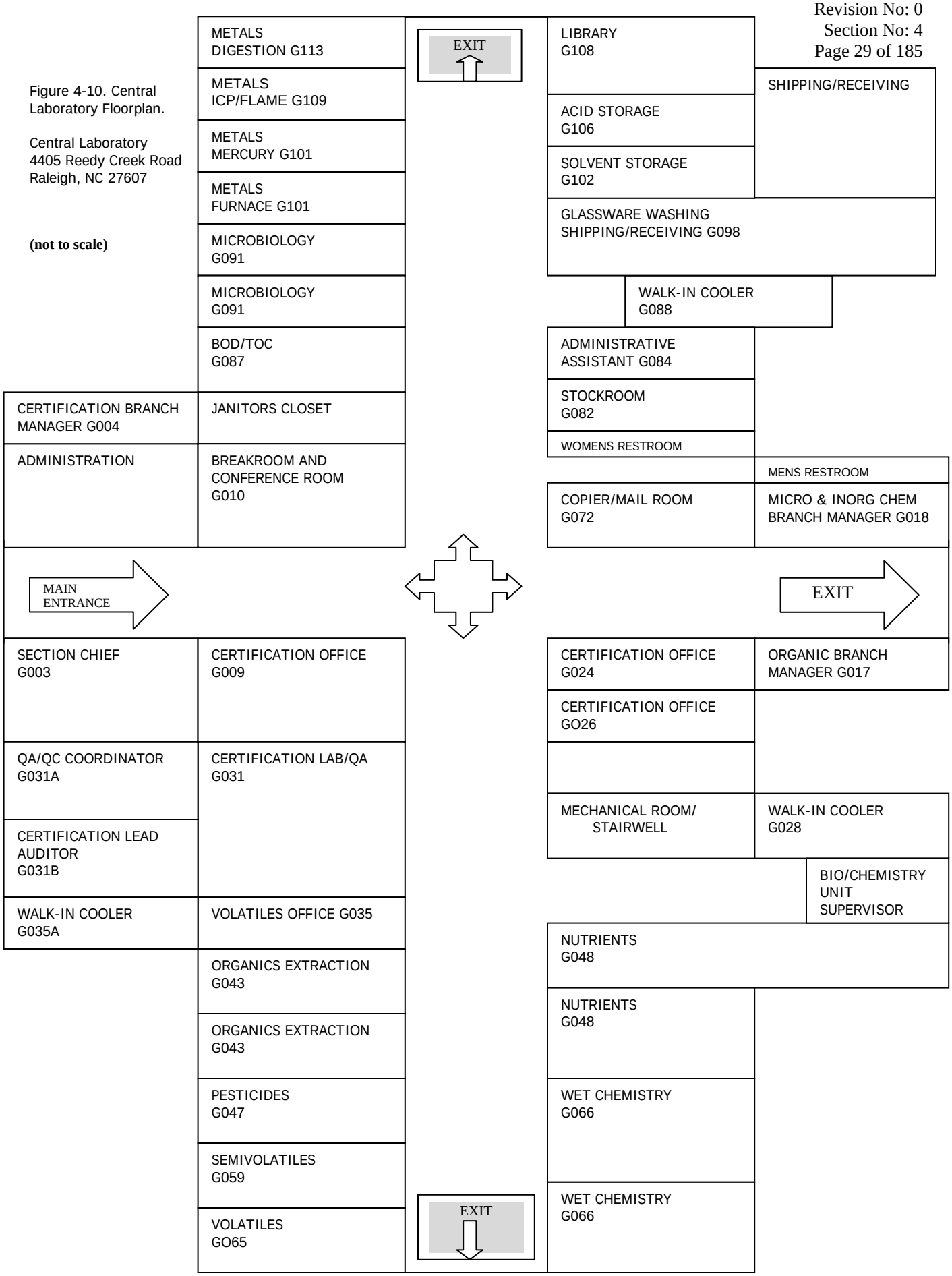


Figure 4-11. Asheville Regional Laboratory Floorplan.

Asheville Laboratory
2090 US Highway 70
Swannanoa, NC 28778

(not to scale)

Lab area is shaded

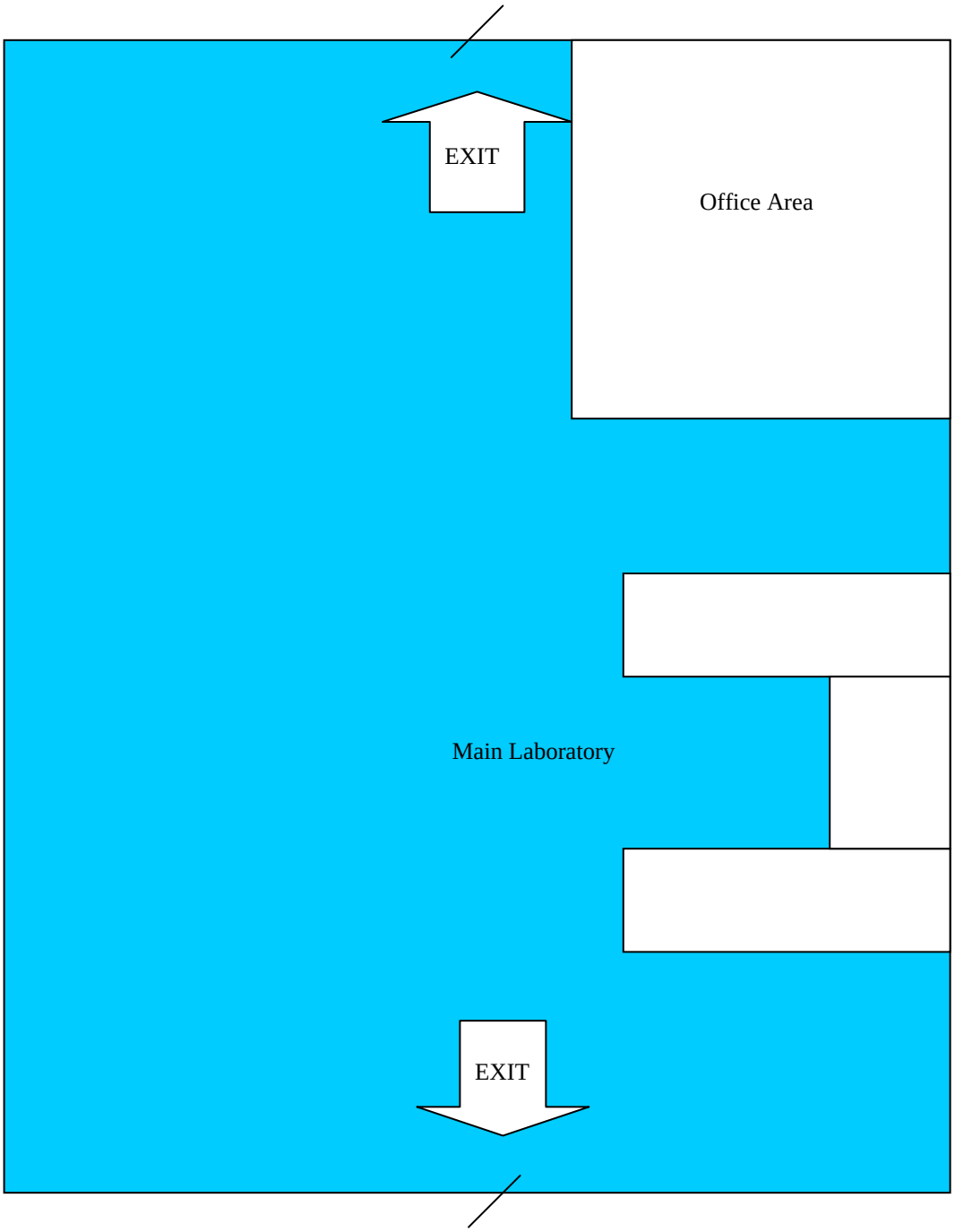


Figure 4-12. Washington Regional Laboratory Floorplan.

Washington Laboratory
943 Washington Square Mall
Washington, NC 27889

(not to scale)

lab area is shaded

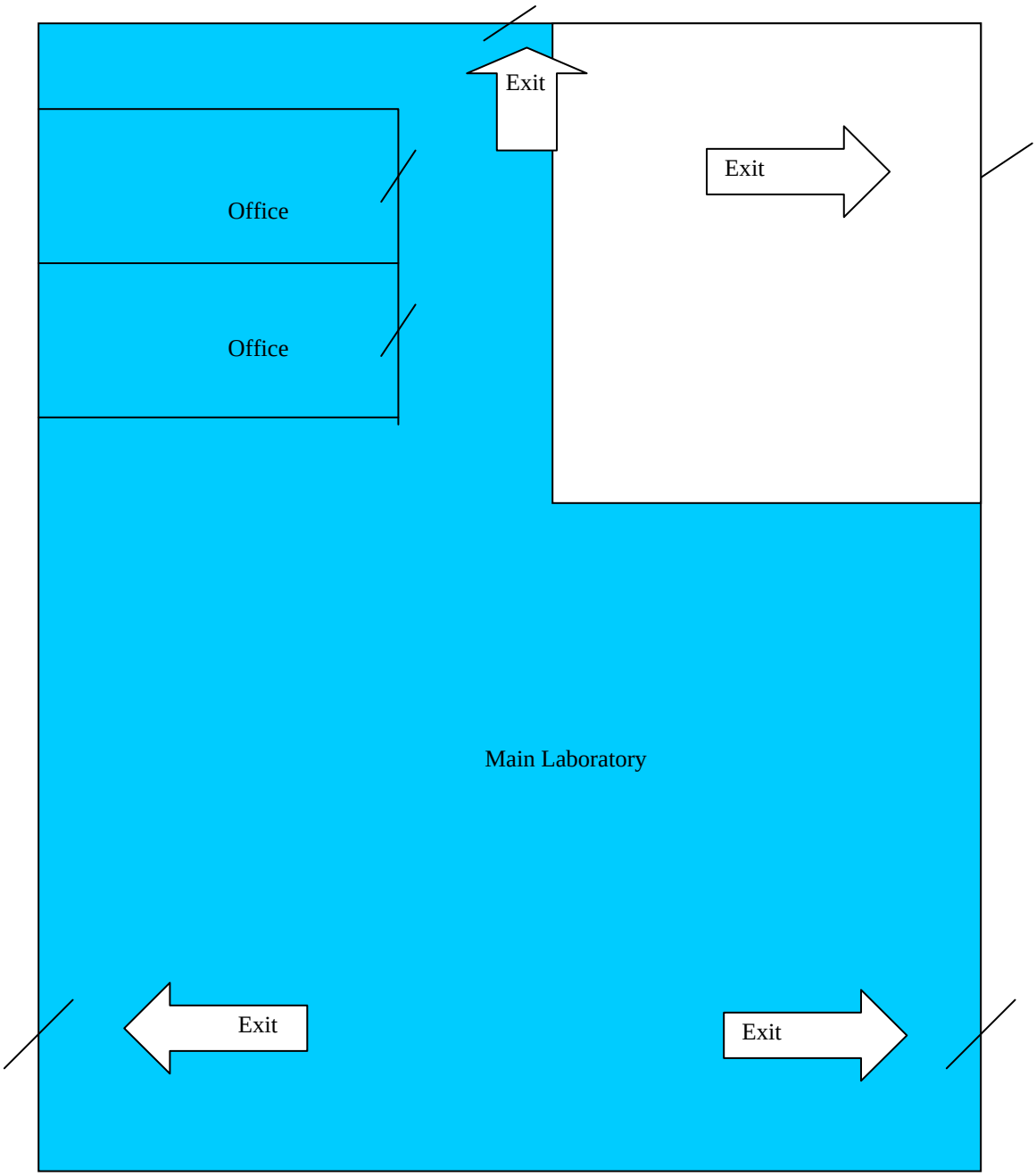


Table 4-1. Central Laboratory Major Equipment List

VOA Equipment	Manufacturer	Model	Serial/ID No.	Year placed in service
GC- ELCD/PID (A)	Hewlett-Packard	5890	2750A16571	1988
Purge and Trap Concentrator	OI Analytical	4460A REV-B	3572-8-286	1988
P&T Autosampler	OI Analytical	MPM16	1988-8-02	1988
GC-ELCD/PID (B)	Hewlett-Packard	5890	2843A19424	1988
Purge and Trap Concentrator	OI Analytical	4460A REV-B	3702-8-294	1988
P&T Autosampler	OI Analytical	MPM16	3793-8-010	1988
GC- PID/FID (C)	Tremetrics	9000	930235	1993
Purge and Trap Concentrator	Tekmar	LSC 2000	92226001	1993
P&T Autosampler	Tekmar	ALS 2016	93041006	1993
GC- ELCD/PID (D)	Hewlett-Packard	5890 Series II Plus	3336A58501	1995
Purge and Trap Concentrator	OI Analytical	4560	3438460079	1995
P&T Autosampler	OI Analytical	MPM16	11203-1-287	1995
GC- ELCD/PID (E)	Finnigan	9001	GC100294	1998
Purge and Trap Concentrator	Tekmar	3000	95132006	1995
P&T Autosampler	Tekmar	ALS 2016	95131001	1995
GC/MS	Agilent	HP5973/6890	US93123009	1999
Purge and Trap Concentrator	Tekmar	3100	00285007	2000
P&T Autosampler	Tekmar	ALS 2016	00304001	2000
XA Computer	Hewlett-Packard	D6720T	US94554773	1999
HP Chemstation software	Hewlett-Packard	G1701BA.02	BN2138C084	1999
Dell Optiplex Computer	Dell	GX240	HJ7HJ11	2002
Total Chrom Software	Perkin-Elmer	TCWS6.2 N515-0511	0502-UP WS0003	2002
GC/Computer Interface	PE Nelson	970A	3290270061	1992
GC/Computer Interface	PE Nelson	970A	3051270236	1992
GC/Computer Linkbox	PE Nelson	610	3047110062	1992
8 Port Terminal Server	Lantronix	ETS8P	8313312	2002
Top Loading Balance	Denver Inst. Co.	XL-500	44656	
Refrigerator	Kenmore			
Refrigerator	Kenmore	5		
SVOA Equipment	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
GC/FID	Hewlett Packard	5890B	2908A21482	1989
GC/FID	Shimadzu	GC17A	C10693101072	1995
GC/MS GC	Agilent	6890	US00038661	2000
GC/MS MS	Agilent	5973N	US03960480	2000
GC/MS GC	Agilent	6890	US00034057	2000
GC/MS MS	Agilent	5973N	US03360393	2000
Analytical Balance	Denver	XE-100A	120001249	1993
Muffle Furnace	Lindberg	51894	899200	1990
Wrist Shaker	Labline	3589-1	11940022	1995
Sonifier	Branson	450	88803021174A	2003
Sonicator	Heat Systems	W-385	G-8179	1987
Freezer	Baxter	U2005XA15	5N6229690	
Freezer	VWR			2003
Freezer	Baxter	U2005XA15	5N6229690	
Freezer	Whirlpool	EEV-203FW0	593413628	

SVOA Equipment, *cont'd.*	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
Top Loading Balance	Denver Instrument Co.	100A	12 001249	1993
Oven	Lindberg		899200	1990
Pesticides Equipment	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
GC/FPD/ECD	Hewlett Packard	5890	2843A20188	1989
GC/NPD/NPD	Tremetrics	9000	920/85	1992
GC/ECD/ECD	Hewlett Packard	5890	2843A20187	1989
GC/ECD/ECD	Tracor	540	871168	1988
Tecator Soxtec	Foss	2050	307880005	2001
Automated Sample Processing System (GPC)	O-I Analytical	AP1000	9254AV	2000
Freezer	VWR	U2020FA14	W08G-350948-WG	1998
Oven	Lindberg/Blue M	G01330A	P27F-295803-PF	1996
Freezer	Labline	FV21M2WLFA	1015392492	1982
GC/FPD/ECD	Tracor	540	861423	1986
GC/ECD/ECD	Tracor	540	84057	1984
Metals Equipment	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
ICP/MS	PerkinElmer	6100	949907	2000
ICP	PerkinElmer	3000XL	069N4121902	1995
AutoSampler	PerkinElmer	AS91	3130	1995
Furnace	PerkinElmer	AAnalyst 800	800S2060103	2002
FIMS	PerkinElmer	FIAS 400	4324	1996
AutoSampler	PerkinElmer	AS90	1305	1991
HotBlock digestion system	Environmental Express	SC100	145CECD310	1999
HotBlock digestion system	Environmental Express	SC100	145CEC0293	1999
Water cooler/recirculator	ISOTemp	1013S	198107070	1998
Argon manifold/ 2 tank hookup	Western	LCHP-7-2	23708	2000
Analytical balance	Mettler	AG204	1121490982	2003
Flow injection/ICPMS	PerkinElmer	FIAS 400	5340	2000
HEPA filtered hood	Environmental Express	SC801	NA	2003
HEPA filtered hood	Environmental Express	SC801	NA	2003
HotBlock digestion system	Environmental Express	SC154	2002CEC1219	2003
Water bath	Blue M	MW-1140A	14957	1986
Water bath	Blue M	MW-1140A	N5-1554	1987
Top loading balance	Fisher	2400-DR	2431	1984
Top loading balance	Denver	XL1800	53725	1994
Hot plate	Barbstead/ Thermodyne	RC2240	41193123888	1994
Hot plate	Barbstead/ Thermodyne	RC2240	411940896575	1995
Water Deionizer	Barbstead/ Thermodyne	D8961	896010867669	2001
Freezer	Kenmore	9203381	VSA1684516	
Nutrients Equipment	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
FIA system with Ammonia	Lachat	QuickChem 8000 series	160878	2001

Nitrogen /Nitrate + Nitrite Nitrogen Manifold				
Nutrients Equipment, *cont'd.*	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
FIA system with TKN Manifold	Lachat	QuickChem 8000 series	160952	2001
FIA system with TP Manifold	Lachat	QuickChem 8000 series	161030	2001
Ion Chromatograph	Lachat	QuickChem 8000 series	160959	2002
Block Digestor	Lachat	BD-46		2001
Block Digestor	Lachat	BD-46		2001
Autoclave	Market Forge	Sterilmatic	166592	2004
PH meter	Fisher Scientific	Accumet Model 15	141979	1996
Centrifuge	Centrific	225	156622	2001
Refrigerator	Kenmore	7674310	E70741344	1980
Top loading balance	Denver Inst. Co.		A42051118	2001
Wet Chemistry Equipment	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
Conductivity Meter	YSI	3100	03B1296	2003
Drill Press, 8" benchtop	Westward	4TM69		2001
UV-Vis Spectrophotometer	Shimadzu	UV1601	A10753983866	2001
UV-Vis Spectrophotometer	Milton Roy	1201	0327833A	1987
Centrifuge	Beckman Coulter	Allegra 6	ALS03A31	2003
UV-Vis Spectrophotometer	Thermo Electron Corp.	Aquamate	114510	2003
Freezer, Explosion-proof	VWR	U2020XA14	025N-622974-ON	2003
Fluorometer	Turner-Designs	10-AU-005-CE	6670R0XX	2003
Fluorometer	Turner-Designs	10-AU-005	5379 FRXX	
Ionanalyzer	Orion	920A	002380	
Analytical Balance	Sartorius	A120S	37100120	1998
Analytical Balance	Mettler	AE200	N61981	1993
Top Load Balance	Ohaus	TS4000	6707	1996
Waterbath	Fisher Scientific	Isotemp 128	107N004-	2002
COD reactor	Hach	45600-02	020300023015	2002
Microbiology Equipment	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
Top Loading Balance	Denver Instrument Co.	XP-3000		
Balance	Denver Instrument Co.	A-200DS	13024400	1993
Quantitray Sampler Sealing System	IDEXX	2X	16096000	2002
Stereo Microscope	Fisher Scientific	Stereo Master	16100000	2002
Stereo Microscope	Fisher Scientific	Stereo Master	16100100	2002
Steri Microscope	Reichert-Jung		13029000	1993
Organic Carbon Analyzer	Tekmar Dohrman	Apollo 9000	15668800	2001
Turbidimeter	HF Scientific	Micro 100	16095400	2002
DO meter	YSI	5100	16195000	2003
ECON Incubator	Precision Scientific	5EM	16098300	2002
Incubator	Curtin Matheson Scientific	Equatherm	10869100	1987
Incubator	Precision Scientific	6LM	13323600	1994
Autoclave	Market Forge	Sterilmatic	16098400	2002
Dry Air Oven	Blue M	Lindberg	14096000	1996
Refrigerator	Kenmore			

Water Bath	Precision	253	14192600	1996
Water Bath	Blue M	Magni World	00579900	
Water Bath	Blue M	Magni World	00150000	
Water Bath	Blue M	Magni World	00149900	
Microbiology Equipment, *cont'd*.	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
Incubator	Sure-Temp	3478-2-Y	DI89216902	1991
Support Equipment	**Manufacturer**	**Model**	**Serial/ID No.**	**Year placed in service**
Autoclave	AMSCO	3201	010539106	1991
Dishwasher	AMSCO	470		1991
Dryer	AMSCO	475		1991
Walk-in cooler (rm. G035-A)	Sure-Temp	3478-2-W	DX89216901	1991
Walk-in cooler (rm. G028)	Sure-Temp	3478-2-W	DX89216902	1991
Walk-in cooler (rm. G088)	Sure-Temp	3478-2-W	DX89216904	1991

Table 4-2. Asheville Regional Laboratory Major Equipment List

Equipment	Manufacturer	Model	Serial/ID No.	Year placed in service
Muffle Furnace	Hotpack	7074	51462	1976
Oven	Blue M	OV-490A-2	JT8798	1976
Oven	Blue M	OV-12A	KAA 8586	1976
Turbidimeter	HF Scientific	Micro 100	201092	2003
DO Meter	YSI	50B	96B46283	1996
pH Meter	Orion	920A	002249	1992
Waterbath	Blue M	MW-1130A-1	MOS-16278	1976
Waterbath	Blue M	MW-1120A-1	M5-5216	1976
Autoclave	Market Forge	STM-E	012105	1976
Analytical Balance	Mettler	AE200	1113052122	1994
Incubator	VWR	2020	1102102	2003
DI water system	Pure Water Solutions		5469	2003
Compound Microscope	Spencer		AROM1	1976

Table 4-3. Washington Regional Laboratory Major Equipment List

Equipment	Manufacturer	Model	Serial/ID No.	Year placed in service
Turbidimeter	Monitek	126-01I-3C	T035	1994
Turbidimeter	HFScientific	Micro 100	211225	2002
Balance	Mettler	H-30	618407	~1975
Balance	Sartorius	MC1, Analytic AC 120 S	20401645	1993
Autoclave	Market Forge	STM-E	14998	~1975
PH meter	Symphony	SB301	0001982	2001
PH meter	Corning	10	D4507	~1975
BOD incubator	Precision	815	699071301	1999
BOD incubator	Shel Lab		0101103	2003
DO Meter	YSI	5000	03C1280	2003
DO Meter	YSI		L8006363	~1998
DO Meter	YSI		91K033108	~1998
Incubator	Blue M	MW-1130A-1	M5-1034	~1975
Incubator	Blue M	MW-1120A-1	M5-5213	~1975
Microscope	American Optical			~1975
Still	Barnstead		8207417	~1975
Oven	Blue M	OV 490A-2	OV3 8829	~1975
Oven	Blue M	OV-12 A		~1975
Oven	Shel Lab		0400103	2003
Oven	Despatch	LEB-1-20	96318	~1975
Muffle Furnace	Lindberg Blue		T29J422375UJ	1998
Incubator	GCA	FREAS 815	19-AF-3	1999

~ Indicates approximate date placed in service.

5.0 QA Targets for Precision, Accuracy and MDLs/PQLs

The DWQ Laboratory 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 demonstrated for the analytical methods on similar samples and to meet data for the analyses published by the US EPA. 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.

5.1.2 Accuracy

The laboratory objective for accuracy is to meet the performance for accuracy demonstrated for the analytical methods on similar samples and to meet the recovery data published by the US EPA. Accuracy is defined as the degree of bias in a measurement system. 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.

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. 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 Laboratory Section 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

Analytes, preparative and analytical methods, matrices, accuracy and precision targets, MDLs and PQLs for analyses performed by the Laboratory Section are presented in Table 5.1. Unless otherwise noted, the limits in these tables are laboratory generated. Some acceptability limits are derived from USEPA methods when they are provided. Where USEPA limits are not provided, the Laboratory Section has 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 Quality Assurance/Quality Control Coordinator and Section Chief's 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 8270).

5.3 Statistically Derived Limits

Statistically derived precision and accuracy limits are required by selected methods and programs. The Laboratory Section will routinely utilize statistically derived limits (based upon laboratory derived data) to evaluate method performance and determine when corrective action may be appropriate. The laboratory may periodically update the limits as stated in this manual. 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 maintains an archive of all limits used within the laboratory. These updated limits may be equal to or tighter than the limits displayed in this QAM. If limits need to be adjusted outside of the limits in this QAM, the QAM will be revised to reflect these changes.

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.

5.4 Method Detection Limits

Method Detection Limits (MDLs) are set such that the risk of reporting a false positive is less than 1%. 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 or any time there is a significant change in laboratory operations.

5.5 Practical Quantitation Limits

Practical Quantitation Limits (PQLs) are set at 3 to 5 times the calculated MDL unless otherwise noted. Because PQL level checks are required, ease of preparation of commercial analytical mixes may dictate to some extent the reported PQL. Generally the PQL is not set at less than 3 times the MDL. However, in some instances, systematic bias (i.e., analyte background in reagents, etc.) necessitates that the reported MDL be elevated to levels that are readily quantifiable. In those instances, the PQL may be set at a level less than three times the reported MDL. Published PQLs may be set higher than experimentally determined PQLs 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 can be reported as required by a client; however, these values are always reported with a qualifier code (N3). Additionally, non-detected analytes are always reported as less than the PQL.

5.6 QA Targets Table

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 all inorganic analyses are within the range of 80 - 120 % for accuracy [except for metals in solid samples, which have been set based on method defined limits (75-125 %)] and < 20% RPD for precision, unless laboratory-generated data indicate that tighter control limits can be routinely maintained. This convention was adopted due to the fact that targets set according to historical data are usually less stringent. The organic QA targets are statutory in nature; Warning and control limits for organic analyses are initially set for groups of compounds based on preliminary method validation data. When additional data is available, the QA targets may be reconsidered. All QA targets are routinely re-evaluated at least annually (and updated, if necessary) against laboratory generated data 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

Table 5.2 lists the keys to the clean up method in Table 5.1.

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 and III.

- **SM##** refers to methods published in *Standard Methods for the Examination of Water and Wastewater*, APHA. Each citation is followed by a two-digit number, which refers specifically to the edition of Standard Methods being cited. For example, **SM18** refers to the 18th Edition (1992), **SM19** refers to the 19th Edition (1995) and **SM20** refers to the 20th Edition (1998).

- **ASTM** refers to methods published in the *Annual Book of ASTM standards*, Vols. 11.01 and 11.02, 1999.

- **HACH** refers to methods published in *Hach Water Analysis Handbook*, 3rd Edition, Hach Company Loveland, CO, 1997.

- **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
QA Targets for Accuracy, Precision and MDLs/PQLs

Metals

Analyte	Prep Method[1]	Analysis Method[2]	Matrix	Spike[3] Recovery Range (%)	QCS[4] Accuracy Range (%)	Precision % RPD	MDL	PQL	Clean-Up Code
	EPA 200.2M/ SM18 3030C	EPA 200.7 / 200.8	W	70 – 130	90-110	≤20	3.10 / 5.78 µg/L	50 µg/L	A
Aluminum	EPA 200.2M	EPA 200.7	S	70 - 130	90-110	≤20	NA[5]	1.0 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8	W	70 – 130	90-110	≤20	0.470 µg/L	10 µg/L	A
Antimony	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 - 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2 M/ SM18 3030C	EPA 200.8 / 200.9	W	70 – 130	90-110	≤20	0.381 / 0.405 µg/L	10 µg/L	A
Arsenic	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M/ SM18 3030C	EPA 200.7	W	70 – 130	90-110	≤20	0.344 µg/L	10 µg/L	A
Barium	EPA 200.2M	EPA 200.8 / 200.7	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8 / 200.7	W	70 – 130	90-110	≤20	0.539 / 0.351 µg/L	10 µg/L	A
Beryllium	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.7	W	70 - 130	90-110	≤20	0.012 mg/L	0.10 mg/kg	A
Calcium	EPA 200.2M	EPA 200.7	S	70 – 130	90-110	≤20	NA[5]	2.0 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8 / 200.9	W	70 – 130	90-110	≤20	0.115 / 0.209µg/L	2.0 µg/L	A
Cadmium	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2 M/ SM18 3030C	EPA 200.8 / 200.7	W	70 – 130	90-110	≤20	0.243 / 0.534 µg/L	25 µg/L	A
Chromium	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8 / 200.7	W	70 – 130	90-110	≤20	0.058 / 0.623 µg/L	50 µg/L	A
Cobalt	EPA 200.2M	EPA 200.8	S	70 - 130	90-110	≤20	NA[5]	1.0 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8 / 200.9	W	70 – 130	90-110	≤20	0.897 / 0.661 µg/L	2.0 µg/L	A
Copper	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.7	W	70 – 130	90-110	≤20	6.19 µg/L	50 µg/L	A
Iron	EPA 200.2M	EPA 200.7	S	70 – 130	90-110	≤20	NA[5]	1.0 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8 / 200.9	W	70 – 130	90-110	≤20	0.091 / 0.737 µg/L	10 µg/L	A
Lead	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 - 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.7	W	70 – 130	90-110	≤20	0.585 µg/L	25 µg/L	A
Lithium	EPA 200.2M	EPA 200.7	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.2 M/ SM18 3030C	EPA 200.7	W	70 – 130	90-110	≤20	0.006 mg/L	0.10 mg/kg	A
Magnesium	EPA 200.2M	EPA 200.7	S	70 – 130	90-110	≤20	NA[5]	2.0 mg/kg	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Metals

Analyte	Prep Method[1]	Analysis Method[2]	Matrix	Spike[3] Recovery Range (%)	QCS[4] Accuracy Range (%)	Precision % RPD	MDL	PQL	Clean-Up Code
	EPA 200.2M / SM18 3030C	EPA 200.7 / 200.8	W	70 – 130	90-110	≤20	0.506 / 0.219 µg/L	10 µg/L	A
Manganese	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 245.1M	EPA 245.1	W	70 – 130	90-110	≤20	0.035 µg/L	0.20 µg/L	A
Mercury	EPA 245.5M	EPA 245.5	S	70 - 130	90-110	≤20	0.004 mg/kg	0.02 mg/kg	A
	EPA 245.6M	EPA 245.6	T	70 – 130	90-110	≤20	0.006 mg/kg	0.02 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8 / 200.9	W	70 – 130	90-110	≤20	0.243 / 2.10 µg/L	10 µg/L	A
Nickel	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.7	W	70 – 130	90-110	≤20	0.006 mg/L	0.10 mg/kg	A
Potassium	EPA 200.2M	EPA 200.7	S	70 – 130	90-110	≤20	NA[5]	2.0 mg/kg	A
	EPA 200.2 M/ SM18 3030C	EPA 200.8 / 200.9	W	70 – 130	90-110	≤20	0.179 / 1.298 µg/L	5.0 µg/L	A
Selenium	EPA 200.2M	EPA 200.8	S	70 - 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.8 / 200.9	W	70 – 130	90-110	≤20	0.277 / 0.967µg/L	5.0 µg/L	A
Silver	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.7	W	70 – 130	90-110	≤20	0.039 mg/L	0.10 mg/kg	A
Sodium	EPA 200.2M	EPA 200.7	S	70 – 130	90-110	≤20	NA[5]	2.0 mg/kg	A
	EPA 200.2 M/ SM18 3030C	EPA 200.8	W	70 – 130	90-110	≤20	0.067 µg/L	10 µg/L	A
Thallium	EPA 200.2M	EPA 200.8	S	70 - 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2 M/ SM18 3030C	EPA 200.7 / 200.8	W	70 – 130	90-110	≤20	0.685 / 1.80 µg/L	25 µg/L	A
Vanadium	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A
	EPA 200.2M / SM18 3030C	EPA 200.7 / 200.8	W	70 – 130	90-110	≤20	1.69 / 2.69 µg/L	10 µg/L	A
Zinc	EPA 200.2M	EPA 200.8	S	70 – 130	90-110	≤20	NA[5]	0.20 mg/kg	A
	EPA 200.3	EPA 200.8	T	70 – 130	90-110	≤20	NA[5]	0.10 mg/kg	A

[1]SM 3030C must be used to prepare aqueous samples taken from groundwater monitoring wells.

[2]Where two methods are listed, the first one is preferred for analysis.

[3]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 1994. EPA Method 200.9, Section 9.4.3, Revision 2.2 May 1994.

[4]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.

[5]NA = not available. MDL values have not been determined for sediment "S" and tissue "T", except for Hg.

* Limits determined from historical data

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Nutrients

Analyte	Prep Method	Analysis Method	Matrix	Spike[1] Accuracy Range (%)	LCS[2] Accuracy Range (%)	Precision % RPD	MDL (ppm)	PQL (ppm)	Clean-Up Code
Ammonia Nitrogen as N	N/A	EPA 350.1 (QUIK CHEM 10-107-06-1-J)	W	90-110	90-110	≤10	0.005	0.01	A
Total Kjeldahl Nitrogen as N	N/A	EPA 351.2 (QUIK CHEM 10-107-06-2-H)	W	80-120 [3]	90-110	≤20 [3]	0.04	0.20	A
Nitrate + Nitrite Nitrogen as N	N/A	EPA 353.2 (QUIK CHEM 10-107-04-1-C)	W	90-110	90-110	≤10	0.004	0.01	A
Phosphorous, Total as P	N/A	EPA 365.1 (QUIK CHEM 10-115-01-1-EF)	W	90-110	90-110	≤10	0.01	0.02	A
Phosphorous, Dissolved as P	N/A	EPA 365.1 (QUIK CHEM 10-115-01-1-EF)	W	90-110	90-110	≤10	0.01	0.02	A
Orthophosphate as P	N/A	EPA 365.1 (QUIK CHEM 10-115-01-1-A)	W	90-110	90-110	≤10	0.01	0.02	A

N/A = not applicable (the preparatory steps for TKN and Phosphorous are incorporated in the Lachat methods.

[1] Quik Chem Lachat Methods

[2] Quik Chem Lachat Methods

[3] SM18 interim until in-house limits are derived.

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Microbiology

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppm or as noted)	PQL (ppm or as noted)	Clean-Up Code
BOD_5	N/A	SM20 5210 B	W	N/A	198 ± 30.5[1]	<20	N/A	2.0	A
Coliform, MF fecal	N/A	SM 189222 D	W	N/A	N/A	<20	N/A	1 cfu/100 ml	A
Coliform, MF total	N/A	SM18 9222 B	W	N/A	N/A	<20	N/A	1 cfu/100 ml	A
Coliform, MPN fecal	N/A	SM 189221 B	W	N/A	N/A	<20	N/A	2 MPN/100 ml	A
Coliform, MPN total	N/A	SM18 9221 B	W	N/A	N/A	<20	N/A	2 MPN/100 ml	A
Coliform, fecal strep	N/A	SM18 9230 C	W	N/A	N/A	<20	N/A	1 cfu/100 ml	A
TOC	N/A	SM18 5310 B	W	80-120	90-110	<20	0.1244	5 mg/L	A
Total residue	N/A	SM18 2540 B	W	N/A	90-110	<20*	N/A	10	A
Total volatile residue	N/A	EPA 160.4	W	N/A	90-110	<20*	N/A	10	A
Total fixed residue	N/A	EPA 160.4	W	N/A	90-110	<20*	N/A	10	A
Total Suspended Residue	N/A	SM18 2540 D	W	N/A	90-110	<20*	N/A	2	A
Total Volatile Suspended Residue	N/A	EPA 160.4	W	N/A	90-110	<20*	N/A	2	A
Total Fixed Suspended Residue	N/A	EPA 160.4	W	N/A	90-110	<20*	N/A	2	A
Turbidity	N/A	SM20 2130 B	W	N/A	90-110	<20	N/A	1 NTU	A

N/A = not applicable
* For concentrations > 50 mg/L
[1] GGA Standard

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Wet Chemistry

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL	PQL	Clean-Up Code
Acidity to pH 4.5	N/A	SM18 2310 B	W	N/A	mfg	≤20		1 mg/L	A
Acidity to pH 8.3	N/A	SM18 2310 B	W	N/A	mfg	≤20		1 mg/L	A
Alkalinity to pH 8.3, total as $CaCO_3$	N/A	SM18 2320 B	W	N/A	mfg	≤20		1 mg/L	A
Alkalinity to pH 4.5, total as $CaCO_3$	N/A	SM18 2320 B	W	N/A	mfg	≤20		1 mg/L	A
Boron	N/A	SM18 4500-B B	W	80-120	mfg	≤20	0.06 ug/L	0.25 ppb	A
Chloride	N/A	EPA 325.3	W	80-120	mfg	≤20	1.68	5 mg/L	A
Chlorophyll *a* (uncorrected)	N/A	EPA 445.0	W	N/A	95-105	≤20	N/A	1 ppb [1]	A
COD	N/A	SM18 5520 D M	W	80-120	mfg	≤20	10.64	20 mg/L	A
Color, ADMI	N/A	SM18 2120 E	W	N/A	80-120	≤20	1.2	25 mg/L	A
Color, True	N/A	SM18 2120 C	W	N/A	80-120	≤20	1.58	5 c.u.	A
Cyanide	SM18 4500-CN C	SM18 4500-CN E	W	80-120	mfg	≤20	0.01	0.02 mg/L	A
Fluoride	SM18 4500-F^- B	SM18 4500-F^- C	W	80-120	mfg	≤20	0.18	0.50 mg/L	A
Formaldehyde	N/A	APHA, 1972 Method 111	W	80-120	80-120	≤20	0.04	0.2 mg/L	A
Grease & Oil	N/A	EPA 1664	W	*	*	*	*	*	A
Hexavalent Chromium	N/A	SM18 3500-Cr D	W	80-120	90-110	≤20	12.45	50 ppb	A
MBAS	N/A	SM18 5540 C	W	80-120	mfg	≤20	0.03	0.1 mg/L	A
Phenol	N/A	EPA 420.1	W	80-120	mfg	≤20	2.94	10 ppb	A
Silica	N/A	USGS 1-1700-85	W	80-120	mfg	≤20	1.8	5 mg/L	A
Specific Conductance	N/A	SM18 2510 B	W	N/A	mfg	≤20	0.31	14.9 umhos/cm	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Wet Chemistry

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL	PQL	Clean-Up Code
Sulfate	N/A	EPA 375.4	W	80-120	mfg	≤20	0.42	5	A
Sulfide	N/A	SM18 4500-S_2 D	W	80-120	mfg	≤20	0.01	0.1	A
Tannin and Lignin	N/A	SM18 5550	W	80-120	mfg	≤20	*	*	A
Total Dissolved Residue	N/A	EPA 160.1	W	80-120	mfg	≤20	N/A	10	A
* Under method development.									
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.									
mfg = Oustide quality control standards are purchased and the manufacturer's published limits are used.									

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Volatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
1,1-Dichloroethene	EPA 5030/601	EPA 8021/601	W	60-150	60-150	≤20	0.03	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.23	1	A
Methylene Chloride	EPA 5030/601	EPA 8021/601	W	59-141	59-141	≤20	0.73	10	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.56	10	A
Trans-1,2-Dichloroethene	EPA 5030/601	EPA 8021/601	W				0.02	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.20	1	A
1,1-Dichloroethane	EPA 5030/601	EPA 8021/601	W				0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.20	1	A
2,2-Dichloropropane	EPA 5030/601	EPA 8021/601	W				0.04	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.37	1	A
cis-1,2-Dichloroethene	EPA 5030/601	EPA 8021/601	W				0.02	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.16	1	A
Chloroform	EPA 5030/601	EPA 8021/601	W	67-133	67-133	≤20	0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.24	1	A
Bromochloromethane	EPA 5030/601	EPA 8021/601	W				0.03	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.31	1	A
1,1,1-Trichloroethane	EPA 5030/601	EPA 8021/601	W	60-141	60-141	≤20	0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.18	1	A
1,1-Dichloropropene	EPA 5030/601	EPA 8021/601	W				0.03	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.15	1	A
Carbon Tetrachloride	EPA 5030/601	EPA 8021/601	W	64-137	64-137	≤20	0.04	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.12	1	A
1,2-Dichloroethane	EPA 5030/601	EPA 8021/601	W	71-133	71-133	≤20	0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.25	1	A
Trichloroethene	EPA 5030/601	EPA 8021/601	W	61-136	61-136	≤20	0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Volatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 5030/624	EPA 8260/624	W				0.19	1	A
1,2-Dichloropropane	EPA 5030/601	EPA 8021/601	W				0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.25	1	A
Bromodichloro-methane	EPA 5030/601	EPA 8021/601	W	71-128	71-128	≤20	0.05	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.26	1	A
Dibromomethane	EPA 5030/601	EPA 8021/601	W				0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.45	1	A
cis-1,3-Dichloropropene	EPA 5030/601	EPA 8021/601	W				0.03	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.19	1	A
trans-1,3-Dichloropropene	EPA 5030/601	EPA 8021/601	W				0.02	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.18	1	A
1,1,2-Trichloroethane	EPA 5030/601	EPA 8021/601	W	66-139	66-139	≤20	0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.45	1	A
Tetrachloroethene	EPA 5030/601	EPA 8021/601	W	62-136	62-136	≤20	0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.08	1	A
1,3-Dichloropropane	EPA 5030/601	EPA 8021/601	W				0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.29	1	A
Dibromochloro-methane	EPA 5030/601	EPA 8021/601	W				0.03	0.30	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.29	1	A
1,2-Dibromoethane	EPA 5030/601	EPA 8021/601	W				0.05	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.21	1	A
Chlorobenzene	EPA 5030/601	EPA 8021/601	W	71-127	71-127	≤20	0.03	0.25	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.15	1	A
1,1,1,2-Tetrachloroethane	EPA 5030/601	EPA 8021/601	W				0.02	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.15	1	A
Bromoform	EPA 5030/601	EPA 8021/601	W	59-139	59-139	≤20	0.04	0.30	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Volatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.36	1	A
1,1,2,2-Tetrachloroethane	EPA 5030/601	EPA 8021/601	W				0.03	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				1.52	5	A
1,2,3-Trichloropropane	EPA 5030/601	EPA 8021/601	W				0.05	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.54	1	A
Bromobenzene	EPA 5030/601/602	EPA 8021/601	W				0.05	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.33	1	A
2-Chlorotoluene	EPA 5030/601/602	EPA 8021/601	W				0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.18	1	A
4-Chlorotoluene	EPA 5030/601/602	EPA 8021/601	W				0.06	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.18	1	A
1,3-Dichlorobenzene	EPA 5030/601/602	EPA 8021/601	W	66-127	66-127	≤20	0.02	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.22	1	A
1,4-Dichlorobenzene	EPA 5030/601/602	EPA 8021/601	W				0.03	0.25	A
	EPA 5030	EPA 8021	S					7.5	A
	EPA 5030/624	EPA 8260/624	W				0.16	1	A
1,2-Dichlorobenzene	EPA 5030/601/602	EPA 8021/601	W	72-124	72-124	≤20	0.06	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.23	1	A
1,2-Dibromo-3-Chloropropane	EPA 5030/601	EPA 8021/601	W				0.08	0.75	A
	EPA 5030	EPA 8021	S					23	A
	EPA 5030/624	EPA 8260/624	W				1.39	5	A
1,2,4-Trichlorobenzene	EPA 5030/601	EPA 8021/601	W				0.04	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.20	1	A
Hexachlorobutadiene	EPA 5030/601	EPA 8021/601	W				0.04	0.30	A
	EPA 5030	EPA 8021	S					9	A
	EPA 5030/624	EPA 8260/624	W				0.25	1	A
1,2,3-Trichlorobenzene	EPA 5030/601	EPA 8021/601	W				0.07	0.75	A
	EPA 5030	EPA 8021	S					23	A
	EPA 5030/624	EPA 8260/624	W				0.29	1	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Volatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
Methyl-tert-butyl ether	EPA 5030/602	EPA 8021/602	W				0.53	5.0	A
	EPA 5030	EPA 8021	S					150	A
	EPA 5030/624	EPA 8260/624	W				1.72	5.0	A
Benzene	EPA 5030/602	EPA 8021/602	W	65-142	65-142	≤20	0.05	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.16	1.0	A
Toluene	EPA 5030/601/602	EPA 8021/602	W	72-126	72-126	≤20	0.09	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.17	1.0	A
Ethyl benzene	EPA 5030/602	EPA 8021/602	W	68-127	68-127	≤20	0.13	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.10	1.0	A
m,p-Xylenes	EPA 5030/602	EPA 8021/602	W				0.17	2.0	A
	EPA 5030	EPA 8021	S					60	A
	EPA 5030/624	EPA 8260/624	W				0.23	2.0	A
o-Xylene	EPA 5030/602	EPA 8021/602	W				0.08	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.11	1.0	A
Styrene	EPA 5030/602	EPA 8021/602	W				0.08	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.14	1.0	A
Isopropylbenzene	EPA 5030/602	EPA 8021/602	W				0.09	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.11	1.0	A
n-Propylbenzene	EPA 5030/602	EPA 8021/602	W				0.08	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.13	1.0	A
1,3,5-Trimethylbenzene	EPA 5030/602	EPA 8021/602	W				0.10	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.19	1.0	A
tert-Butylbenzene	EPA 5030/602	EPA 8021/602	W				0.11	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.16	1.0	A
1,2,4-Trimethylbenzene	EPA 5030/602	EPA 8021/602	W				0.09	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.18	1.0	A
sec-Butylbenzene	EPA 5030/602	EPA 8021/602	W				0.10	1.0	A
	EPA 5030	EPA 8021	S					30	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Volatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 5030/624	EPA 8260/624	W				0.12	1.0	A
p-isopropyltoluene	EPA 5030/602	EPA 8021/602	W				0.11	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.16	1.0	A
n-Butylbenzene	EPA 5030/602	EPA 8021/602	W				0.10	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				0.14	1.0	A
Naphthalene	EPA 5030/602	EPA 8021/602	W				0.10	1.0	A
	EPA 5030	EPA 8021	S					30	A
	EPA 5030/624	EPA 8260/624	W				025	2.0	A
								PPM	
TPH-GRO	EPA 5030	CA LUFT	W				0.02	0.2	A
	EPA 5030	CA LUFT	S					6	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Semivolatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
ANILINE	EPA 625/3510	EPA 625/8270	W				4	10	A
	EPA 3550	EPA 8270	S				260	660	A
PHENOL	EPA 625/3510	EPA 625/8270	W	15 - 55	15 - 55	≤22	4	10	A
	EPA 3550	EPA 8270	S	26 - 90	26 - 90	≤35	260	660	A
BIS(2-CHLOROETHYL) ETHER	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2-CHLOROPHENOL	EPA 625/3510	EPA 625/8270	W	49 – 93	49 – 93	≤16	2	10	A
	EPA 3550	EPA 8270	S	25 – 102	25 – 102	≤50	130	660	A
1,3-DICHLOROBENZENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
1,4-DICHLOROBENZENE	EPA 625/3510	EPA 625/8270	W	41 - 92	41 - 92	≤22	2	10	A
	EPA 3550	EPA 8270	S	28 - 104	28 - 104	≤27	130	660	A
BENZYL ALCOHOL	EPA 625/3510	EPA 625/8270	W				4	20	A
	EPA 3550	EPA 8270	S				260	1300	A
1,2-DICHLOROBENZENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2-METHYL PHENOL	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
BIS(2-CHLOROISOPROPYL) ETHER	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
4-METHYL PHENOL	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
N-NITROSO-DI-N-PROPYLAMINE	EPA 625/3510	EPA 625/8270	W	55 - 107	55 - 107	≤17	2	10	A
	EPA 3550	EPA 8270	S	41 - 126	41 - 126	≤38	130	660	A
HEXACHLORO-ETHANE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
NITROBENZENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
ISOPHORONE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2-NITRO PHENOL	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2,4-DIMETHYL PHENOL	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				200	660	A
BENZOIC ACID	EPA 625/3510	EPA 625/8270	W				10	50	A
	EPA 3550	EPA 8270	S				660	3300	A
BIS(2-CHLOROETHOXY) METHANE	EPA 625/3510	EPA 625/8270	W				2	10	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Semivolatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 3550	EPA 8270	S				130	660	A
2,4-DICHLORO PHENOL	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
1,2,4-TRICHLORO-BENZENE	EPA 625/3510	EPA 625/8270	W	43 - 94	43 - 94	≤21	2	10	A
	EPA 3550	EPA 8270	S	38 – 107	38 - 107	≤23	130	660	A
NAPHTHALENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
4-CHLOROANILINE	EPA 625/3510	EPA 625/8270	W				4	20	A
	EPA 3550	EPA 8270	S				330	1300	A
HEXACHLORO-BUTADIENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
4-CHLORO-3-METHYL PHENOL	EPA 625/3510	EPA 625/8270	W	48 - 104	48 - 104	≤15	2	10	A
	EPA 3550	EPA 8270	S	26 - 103	26 - 103	≤33	130	660	A
2-METHYL NAPHTHALENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
HEXACHLORO-CYCLOPENTADIENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2,4,6-TRICHLORO PHENOL	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2,4,5-TRICHLORO PHENOL	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2-CHLORO NAPHTHALENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2-NITROANILINE	EPA 625/3510	EPA 625/8270	W				10	50	A
	EPA 3550	EPA 8270	S				660	3300	A
DIMETHYL PHTHALATE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
ACENAPHTHYLENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2,6-DINITROTOLUENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
3-NITROANILINE	EPA 625/3510	EPA 625/8270	W				10	50	A
	EPA 3550	EPA 8270	S				660	3300	A
ACENAPHTHENE	EPA 625/3510	EPA 625/8270	W	47 - 102	47 - 102	≤20	2	10	A
	EPA 3550	EPA 8270	S	31 - 137	31 - 137	≤19	130	660	A
2,4-DINITRO PHENOL	EPA 625/3510	EPA 625/8270	W				10	50	A
	EPA 3550	EPA 8270	S				660	3300	A
4-NITRO PHENOL	EPA 625/3510	EPA 625/8270	W	14 - 69	14 - 69	≤33	10	50	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Semivolatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 3550	EPA 8270	S	11 - 114	11 - 114	≤50	660	3300	A
DIBENZOFURAN	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
2,4-DINITROTOLUENE	EPA 625/3510	EPA 625/8270	W	41 - 103	41 - 103	≤17	2	10	A
	EPA 3550	EPA 8270	S	28 - 89	28 - 89	≤47	130	660	A
DIETHYL PHTHALATE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
4-CHLOROPHENYL PHENYL ETHER	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
FLUORENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
4-NITROANILINE	EPA 625/3510	EPA 625/8270	W				10	50	A
	EPA 3550	EPA 8270	S				660	3300	A
4,6-DINITRO-2-METHYL PHENOL	EPA 625/3510	EPA 625/8270	W				10	50	A
	EPA 3550	EPA 8270	S				660	3300	A
N-NITROSODI-PHENYLAMINE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
4-BROMOPHENYL PHENYL ETHER	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
HEXACHLORO-BENZENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
PENTACHLORO- PHENOL	EPA 625/3510	EPA 625/8270	W	46 - 122	46 - 122	≤18	10	50	A
	EPA 3550	EPA 8270	S	17 - 109	17 - 109	≤47	660	3300	A
PHENANTHRENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
ANTHRACENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
DI-N-BUTYL PHTHALATE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
FLUORANTHENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
PYRENE	EPA 625/3510	EPA 625/8270	W	47 - 100	47 - 100	≤27	2	10	A
	EPA 3550	EPA 8270	S	35 - 142	35 - 142	≤36	130	660	A
BUTYLBENZYL PHTHALATE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
3,3'-DICHLORO-BENZIDINE	EPA 625/3510	EPA 625/8270	W				5	20	A
	EPA 3550	EPA 8270	S				260	1300	A
BENZO(A)-ANTHRACENE	EPA 625/3510	EPA 625/8270	W				2	10	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Semivolatile Organics

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 3550	EPA 8270	S				130	660	A
CHRYSENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
BIS(2-ETHYLHEXYL) PHTHALATE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
DI-N-OCTYL PHTHALATE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
BENZO(B)-FLUORANTHENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
BENZO(K)-FLUORANTHENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
BENZO(A)PYRENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
INDENO(1,2,3-CD)-PYRENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
DIBENZO(A,H)-ANTHRACENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
BENZO(G,H,I)-PERYLENE	EPA 625/3510	EPA 625/8270	W				2	10	A
	EPA 3550	EPA 8270	S				130	660	A
TPH - DRO	EPA 3500	CA LUFT	W	12 - 127	12 - 127	≤45	0.05 mg/L	0.5 mg/L	A
	EPA 3550	CA LUFT	S	36 - 119	55 - 110	≤45	2 mg/Kg	10 mg/Kg	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Acid Herbicides (ECD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
ACIFLUORFEN (BLAZER)	EPA515.1, 8151A	EPA 8151A, 8000B	W				.04	0.1	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				.71	3.3	A
BENTAZON	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.05	0.3	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				1.5	13	A
CHLORAMBEN	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.02	0.1	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				.94	3.3	A
2,4-D	EPA 515.1, 8151A	EPA 8151A, 8000B	W	30-142	30-142	≤35	.09	0.4	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S	39-146	39-146	≤30	2.56	6.7	A
2,4-DB	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.23	0.7	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				3.9	27	A
DCPA (ACID METABOLITES)	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.12	0.4	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				NE	NE	A
DICAMBA	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.07	0.2	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				1.2	3.3	A
3,5 DICHLOROBENZOIC ACID	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.1	0.5	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				1.16	3.3	A
DICHLORPROP	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.11	0.5	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				6.38	20	A
DINOSEB	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.08	0.2	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				2.02	6.7	A
5-HYDROXYDICAMBA	EPA 515.1, 8151A	EPA 8151A, 8000B	W				NA	NA	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				NA	NA	A
4-NITROPHENOL	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.21	0.6	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				NE	13	A
PENTACHLORO-PHENOL (PCP)	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.05	0.1	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				.7	3.3	A
PICLORAM	EPA 515.1, 8151A	EPA 8151A, 8000B	W				.1	0.3	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S				.86	6.7	A
2,4,5- T	EPA 515.1, 8151A	EPA 8151A, 8000B	W	30-131	30-131	≤26	.04	0.1	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S	23-143	23-143	≤30	.87	3.3	A
2,4,5-TP (SILVEX)	EPA 515.1, 8151A	EPA 8151A, 8000B	W	41-117	41-117	≤21	.04	0.1	A
	EPA 515.1, 8151A	EPA 8151A, 8000B	S	10-134	10-134	≤30			A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Chlorinated Pesticides/PCBs (ECD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
ALACHLOR	EPA 3510C	EPA 8081A	W					0.15	A
	EPA 3550	EPA 8081A	S					5.0	A
ALDRIN	EPA 3510C	EPA 8081A	W	47-113	47-113	≤21	.01	.025	A
	EPA 3550	EPA 8081A	S	44-135	44-135	≤43		0.83	A
ATRAZINE	EPA 3510C	EPA 8081A	W					3.0	A
	EPA 3550	EPA 8081A	S					100	A
BHC-ALPHA	EPA 3510C	EPA 8081A	W				.01	.025	A
	EPA 3550	EPA 8081A	S					0.83	A
BHC-BETA	EPA 3510C	EPA 8081A	W				.01	.025	A
	EPA 3550	EPA 8081A	S					0.83	A
BHC-DELTA	EPA 3510C	EPA 8081A	W				.01	.025	A
	EPA 3550	EPA 8081A	S					0.83	A
BHC-GAMMA (LINDANE)	EPA 3510C	EPA 8081A	W	42-126	42-126	≤21	.01	.025	A
	EPA 3550	EPA 8081A	S	47-118	47-118	≤50		0.83	A
CHLORDANE, TECHNICAL	EPA 3510C	EPA 8081A	W					0.50	A
	EPA 3550	EPA 8081A	S					17	A
CHLORDANE-ALPHA	EPA 3510C	EPA 8081A	W					0.020	A
	EPA 3550	EPA 8081A	S					0.50	A
CHLORDANE-GAMMA	EPA 3510C	EPA 8081A	W					0.020	A
	EPA 3550	EPA 8081A	S					0.50	A
CHLORDENE	EPA 3510C	EPA 8081A	W					0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
CHLORNEB	EPA 3510C	EPA 8081A	W					0.20	A
	EPA 3550	EPA 8081A	S					6.7	A
CHLOROBENZILATE	EPA 3510C	EPA 8081A	W					0.60	A
	EPA 3550	EPA 8081A	S					20	A
CHLORPYRIFOS	EPA 3510C	EPA 8081A	W					0.050	A
	EPA 3550	EPA 8081A	S					1.7	A
CHLOROTHALONIL	EPA 3510C	EPA 8081A	W					0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
DCPA	EPA 3510C	EPA 8081A	W					0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
DDD, OP	EPA 3510C	EPA 8081A	W					0.050	A
	EPA 3550	EPA 8081A	S					1.7	A
DDD, PP	EPA 3510C	EPA 8081A	W				.01	0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
DDE, OP	EPA 3510C	EPA 8081A	W					0.040	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Chlorinated Pesticides/PCBs (ECD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 3550	EPA 8081A	S					1.3	A
DDE, PP	EPA 3510C	EPA 8081A	W				.03	0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
DDT, OP	EPA 3510C	EPA 8081A	W					0.030	A
	EPA 3550	EPA 8081A	S					1.0	A
DDT, PP	EPA 3510C	EPA 8081A	W	35-137	35.137	≤24	.03	0.025	A
	EPA 3550	EPA 8081A	S	29-185	29-185	≤50		0.83	A
DIELDRIN	EPA 3510C	EPA 8081A	W	27-149	27-149	≤39	.03	0.025	A
	EPA 3550	EPA 8081A	S	54-127	54-127	≤48		0.83	A
ENDOSULFAN I	EPA 3510C	EPA 8081A	W				.01	0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
ENDOSULFAN II	EPA 3510C	EPA 8081A	W				.01	0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
ENDOSULFAN SULFATE	EPA 3510C	EPA 8081A	W				.03	0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
ENDRIN	EPA 3510C	EPA 8081A	W	47-117	47-117	≤23	.01	0.025	A
	EPA 3550	EPA 8081A	S	44-120	44-120	≤45		0.83	A
ENDRIN ANDEHYDE	EPA 3510C	EPA 8081A	W				.01	0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
ENDRIN KETONE	EPA 3510C	EPA 8081A	W					0.030	A
	EPA 3550	EPA 8081A	S					1.0	A
ETHAZOLE	EPA 3510C	EPA 8081A	W					0.060	A
	EPA 3550	EPA 8081A	S					2.0	A
HEPTACHLOR	EPA 3510C	EPA 8081A	W	41-122	41-122	≤25	.01	0.025	A
	EPA 3550	EPA 8081A	S	37-130	37-130	≤31		0.83	A
HEPTACHLOR EPOXIDE	EPA 3510C	EPA 8081A	W				.01	0.025	A
	EPA 3550	EPA 8081A	S					0.83	A
HEXACHLORO-BENZENE	EPA 3510C	EPA 8081A	W					0.015	A
	EPA 3550	EPA 8081A	S					0.50	A
MALATHION	EPA 3510C	EPA 8081A	W					0.20	A
	EPA 3550	EPA 8081A	S					6.7	A
METHOXYCHLOR, PP	EPA 3510C	EPA 8081A	W					0.10	A
	EPA 3550	EPA 8081A	S					3.3	A
MIREX	EPA 3510C	EPA 8081A	W					0.030	A
	EPA 3550	EPA 8081A	S					1.0	A
TRANS-NONACHLOR	EPA 3510C	EPA 8081A	W					0.020	A
	EPA 3550	EPA 8081A	S					0.50	A
OXYCHLORDANE	EPA 3510C	EPA 8081A	W					0.050	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Chlorinated Pesticides/PCBs (ECD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 3550	EPA 8081A	S					1.70	A
MIXED-PERMETHRIN	EPA 3510C	EPA 8081A	W					1.20	A
	EPA 3550	EPA 8081A	S					40	A
PROPACHLOR	EPA 3510C	EPA 8081A	W					0.30	A
	EPA 3550	EPA 8081A	S					10.0	A
TECNAZENE	EPA 3510C	EPA 8081A	W					0.010	A
	EPA 3550	EPA 8081A	S					0.33	A
TRIFLURALIN	EPA 3510C	EPA 8081A	W					0.035	A
	EPA 3550	EPA 8081A	S					1.2	A
AROCHLOR 1016	EPA 3510C	EPA 8082	W	50-150	50-150	≤20		1.0	A
	EPA 3550	EPA 8082	S	50-150	50-150	≤30		33	A
AROCHLOR 1021	EPA 3510C	EPA 8082	W					1.0	A
	EPA 3550	EPA 8082	S					33	A
AROCHLOR 1032	EPA 3510C	EPA 8082	W					1.0	A
	EPA 3550	EPA 8082	S					33	A
AROCHLOR 1042	EPA 3510C	EPA 8082	W					1.0	A
	EPA 3550	EPA 8082	S					33	A
AROCHLOR 1048	EPA 3510C	EPA 8082	W					1.0	A
	EPA 3550	EPA 8082	S					33	A
AROCHLOR 1054	EPA 3510C	EPA 8082	W					1.0	A
	EPA 3550	EPA 8082	S					33	A
AROCHLOR 1260	EPA 3510C	EPA 8082	W	50-150	50-150	≤20		1.0	A
	EPA 3550	EPA 8082	S	50-150	50-150	≤30		33	A
AROCHLOR 1262	EPA 3510C	EPA 8082	W					1.0	A
	EPA 3550	EPA 8082	S					33	A
TOXAPHENE	EPA 3510C	EPA 8081A	W					3.0	A
	EPA 3550	EPA 8081A	S					100	A

Table 5.1
QA Targets for Accuracy, Precision and MDL's/PQL's

Nitrogen Pesticides (NPD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
ALACHLOR	EPA 3510C	EPA 619	W				1.6	15	A
	EPA 3550	EPA 619	S					500	A
AMETRYN	EPA 3510C	EPA 619	W				1.1	4.5	A
	EPA 3550	EPA 619	S					150	A
ATRAZINE	EPA 3510C	EPA 619	W				1.1	4.5	A
	EPA 3550	EPA 619	S					150	A
BROMACIL	EPA 3510C	EPA 619	W				4.6	15	A
	EPA 3550	EPA 619	S					500	A
BUTACHLOR	EPA 3510C	EPA 619	W					15	A
	EPA 3550	EPA 619	S					500	A
BUTYLATE	EPA 3510C	EPA 619	W				0.56*	4.5	A
	EPA 3550	EPA 619	S					150	A
CARBOXIN	EPA 3510C	EPA 619	W				3.9	15	A
	EPA 3550	EPA 619	S					500	A
CHLORPROPHAM	EPA 3510C	EPA 619	W				2.6	15	A
	EPA 3550	EPA 619	S					500	A
CHLORPYRIFOS	EPA 3510C	EPA 619	W				0.56	1.5	A
	EPA 3550	EPA 619	S					50	A
CYANAZINE	EPA 3510C	EPA 619	W					15	A
	EPA 3550	EPA 619	S					500	A
CYCLOATE	EPA 3510C	EPA 619	W				.96	4.5	A
	EPA 3550	EPA 619	S					150	A
DIAZINON	EPA 3510C	EPA 619	W				11*	15	A
	EPA 3550	EPA 619	S					500	A
DIPHENAMID	EPA 3510C	EPA 619	W				1.8	15	A
	EPA 3550	EPA 619	S					500	A
EPTC (EPTAM)	EPA 3510C	EPA 619	W				0.45	4.5	A
	EPA 3550	EPA 619	S					150	A
FENAMIPHOS	EPA 3510C	EPA 619	W				4.0	15	A
	EPA 3550	EPA 619	S					500	A
HEXAZINONE	EPA 3510C	EPA 619	W				7.3*	15	A
	EPA 3550	EPA 619	S					500	A
METOLACHLOR	EPA 3510C	EPA 619	W					15	A
	EPA 3550	EPA 619	S					500	A
METRIBUZIN	EPA 3510C	EPA 619	W				2.1	15	A
	EPA 3550	EPA 619	S					500	A
MGK 264	EPA 3510C	EPA 619	W					30	A

Table 5.1
QA Targets for Accuracy, Precision and MDL's/PQL's

Nitrogen Pesticides (NPD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
	EPA 3550	EPA 619	S					1000	A
MOLINATE	EPA 3510C	EPA 619	W				0.40*	4.5	A
	EPA 3550	EPA 619	S					150	A
NAPROPAMIDE	EPA 3510C	EPA 619	W					15	A
	EPA 3550	EPA 619	S					500	A
NORFLURAZON	EPA 3510C	EPA 619	W				2.3	15	A
	EPA 3550	EPA 619	S					500	A
PEBULATE	EPA 3510C	EPA 619	W				0.54	4.5	A
	EPA 3550	EPA 619	S					150	A
PROMETON	EPA 3510C	EPA 619	W				0.62	4.5	A
	EPA 3550	EPA 619	S					150	A
PROMETRYN	EPA 3510C	EPA 619	W				1.5	4.5	A
	EPA 3550	EPA 619	S					150	A
PRONAMIDE	EPA 3510C	EPA 619	W					15	A
	EPA 3550	EPA 619	S					500	A
PROPAZINE	EPA 3510C	EPA 619	W				0.56	4.5	A
	EPA 3550	EPA 619	S					150	A
SIMAZINE	EPA 3510C	EPA 619	W	63-143	63-143	19	0.96	4.5	A
	EPA 3550	EPA 619	S	50-126	50-126	30		150	A
SIMETRYN	EPA 3510C	EPA 619	W				0.72	4.5	A
	EPA 3550	EPA 619	S					150	A
TEBUTHIURON	EPA 3510C	EPA 619	W				4.0	15	A
	EPA 3550	EPA 619	S					500	A
TERBACIL	EPA 3510C	EPA 619	W				10	30	A
	EPA 3550	EPA 619	S					1000	A
TERBUFOS	EPA 3510C	EPA 619	W					15	A
	EPA 3550	EPA 619	S					500	A
TERBUTRYN	EPA 3510C	EPA 619	W				1.1	4.5	A
	EPA 3550	EPA 619	S					150	A
VERNOLATE	EPA 3510C	EPA 619	W	65-141	65-141	20	1.1*	4.5	A
	EPA 3550	EPA 619	S	68-124	68-124	30		150	A
*Interim values.									

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Organophosphorous Pesticides (FPD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
CARBOPHENOTHION	EPA 3510C	EPA 8141A	W				.30	.80	A
	EPA 3550	EPA 8141A	S				2.9	27	A
CHLORPYRIFOS	EPA 3510C	EPA 8141A	W				.16	.40	A
	EPA 3550	EPA 8141A	S				2.0	13	A
DEF	EPA 3510C	EPA 8141A	W				.33	.40	A
	EPA 3550	EPA 8141A	S				3.0	13	A
DEMETON	EPA 3510C	EPA 8141A	W				NE	.80	A
	EPA 3550	EPA 8141A	S				NE	27	A
DIAZINON	EPA 3510C	EPA 8141A	W	51-124	51-124	≤25	.25	.40	A
	EPA 3550	EPA 8141A	S	34-153	34-153	≤30	1.8	13	A
DICHLORVOS	EPA 3510C	EPA 8141A	W				.85	2.1	A
	EPA 3550	EPA 8141A	S				7.1	13	A
DIMETHOATE	EPA 3510C	EPA 8141A	W				.24	.40	A
	EPA 3550	EPA 8141A	S				2.0	13	A
DISULFOTON	EPA 3510C	EPA 8141A	W				NE	.80	A
	EPA 3550	EPA 8141A	S				NE	27	A
DISULFOTON SULFONE	EPA 3510C	EPA 8141A	W				NE	1.0	A
	EPA 3550	EPA 8141A	S				NE	33	A
DISULFOTON SULFOXIDE	EPA 3510C	EPA 8141A	W				NE	NE	A
	EPA 3550	EPA 8141A	S				NE	NE	A
EPN	EPA 3510C	EPA 8141A	W	42-133	42-133	≤38	.22	.40	A
	EPA 3550	EPA 8141A	S	72-117	72-117	≤30	1.8	13	A
ETHION	EPA 3510C	EPA 8141A	W				.17	.40	A
	EPA 3550	EPA 8141A	S				2.5	13	A
ETHOPROP	EPA 3510C	EPA 8141A	W				.29	.40	A
	EPA 3550	EPA 8141A	S				1.2	13	A
FENTHION	EPA 3510C	EPA 8141A	W	18-140	18-140	≤30	.40	.40	A
	EPA 3550	EPA 8141A	S	61-110	61-110	≤30	1.1	13	A
FENSULFOTHION	EPA 3510C	EPA 8141A	W				2.0	2.2	A
	EPA 3550	EPA 8141A	S				5.5	16	A
FOLEX (MERPHOS, TRIBUFOS)	EPA 3510C	EPA 8141A	W				NA	NA	A
	EPA 3550	EPA 8141A	S				NA	NA	A
MEVINPHOS	EPA 3510C	EPA 8141A	W				.42	.40	A
	EPA 3550	EPA 8141A	S				3.7	13	A
MONOCROTOPHOS	EPA 3510C	EPA 8141A	W				NE	1.0	A
	EPA 3550	EPA 8141A	S				NE	33	A

Table 5.1
QA Targets for Accuracy, Precision and MDLs/PQLs

Organophosphorous Pesticides (FPD)

Analyte	Prep Method	Analysis Method	Matrix	Spike Accuracy Range (%)	LCS Accuracy Range (%)	Precision % RPD	MDL (ppb)	PQL (ppb)	Clean-Up Code
NALED	EPA 3510C	EPA 8141A	W				1.02	2.7	A
	EPA 3550	EPA 8141A	S				11.4	NE	A
ETHYL PARATHION	EPA 3510C	EPA 8141A	W				.28	.40	A
	EPA 3550	EPA 8141A	S				2.9	13	A
METHYL PARATHION	EPA 3510C	EPA 8141A	W				.16	.40	A
	EPA 3550	EPA 8141A	S				1.5	13	A
PHORATE	EPA 3510C	EPA 8141A	W				NE	.40	A
	EPA 3550	EPA 8141A	S				NE	13	A
RONNEL	EPA 3510C	EPA 8141A	W				.17	.40	A
	EPA 3550	EPA 8141A	S				1.6	13	A
SULFOTEPP	EPA 3510C	EPA 8141A	W				NE	.40	A
	EPA 3550	EPA 8141A	S				NE	13	A
TERBUFOS	EPA 3510C	EPA 8141A	W				NE	.40	A
	EPA 3550	EPA 8141A	S				NE	13	A

Table 5.2 Key to Clean-up Procedures

Code	Definition
A	Not applicable
B	Clean up included in preparation or analysis method
C	EPA 3660A (Sulfur clean-up)
D	EPA 3620 (Florisil clean-up)
E	EPA 3665 (Sulfuric Acid clean-up)

6.0 Sampling Procedures

The DWQ Laboratory Section does not provide field-sampling services. The laboratory's responsibility in the sample collection process lies in supplying the sampler with proper containers and preservatives. The Laboratory Section welcomes consultation with collectors for whatever assistance can be provided.

6.1 Sampling Containers

6.1.1 Sampling Container Sources

The Laboratory Section 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 Table 8-1 are followed.

The sources for all bottles are:

(a) Carolina Food (Shelburne Plastics) - variety of inorganic analyses
(b) Eagle Picher - VOA
(c) Nalge® - BOD, Coliform, Chlorophyll, Cyanide
(d) Qorpak® - Total Phenol
(e) 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
(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

6.2 Preservatives

Upon request, preservatives are provided to field sampling personnel in bottles or in sealed pre-scored ampoules. In some cases, preservatives supplied directly from a private vendor are drop-shipped to the regional offices. The sodium thiosulfate preservative for coliform samples is supplied by the Central Laboratory support personnel in pre-cleaned, sterilized sampling 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

The Laboratory Section 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, 500 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 Table 8-1. The cleaned bottles are stored in the Sample Shipping/Receiving area (G-098) of the laboratory away from laboratory activities.

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 Quality) and 6.2 (Groundwater). These tables are adapted from *40 CFR, Chapter 1, Part 136, Table II*. 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 III*. Tissue samples are collected, filleted and frozen in metal tins prior to submission to the laboratory. Tissue samples are frozen indefinitely until preparation and 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 or Sample Anomaly Report (SAR). If criteria are not specified in a source document, internal DWQ Laboratory Section guidelines have been set and are footnoted in the tables.

"Analyze immediately" is an EPA designation reserved for tests which, for compliance monitoring projects, should be performed by field instrumentation or a laboratory " within 15 minutes or less" of sampling. The Laboratory Section does not perform these 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 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.

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.

6.4.1.3 Inorganics and Metals

For inorganics and metals analysis, with the exception noted below, 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 incubation begins.

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 the Sample Tracking and Reporting Laboratory Information Management System (DWQ STAR LIMS) and assigning tests. The Branch Manager or Supervisor is 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 increased emphasis on emergency and enforcement actions, it is imperative that the laboratories meet all holding and incubation times. In order to properly process samples and keep overtime to a minimum, the Central Laboratory has established the following times for receipt of samples:

1. Samples for BOD, PO_4, Metals (Groundwater), Turbidity, Color, MBAS, and MF coliform analysis will not be accepted after 1:00 pm on Fridays and workdays that immediately precede a holiday. Employees planning to submit more than six samples on these days for these parameters should contact the laboratory to schedule the samples in advance.

2. MF coliform samples expected to meet the required six-hour holding time will not be accepted after 3:00 pm on normal Monday through Thursday workdays. Employees planning to submit more than five coliform samples in this category should contact the Bio/Chemistry Unit Supervisor to schedule the sample in advance.

3. All Tube coliform samples must be scheduled in advance by contacting the Bio/Chemistry Unit Supervisor.

4. Chlorophyll samples should not be submitted after 3:00 PM on any day since these must be filtered on the day of receipt, regardless of holding time.

5. Unpreserved samples for individual analysis of nitrate or nitrite should be scheduled with Cindy Green 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. A concurrent preserved nutrients sample should be submitted for which nitrate+nitrite analysis has been requested.

The Asheville and Washington Regional Laboratories have similar policies, but tend to communicate daily with their samplers so allowances are often made based upon verbal agreements. The Asheville Regional laboratory has established the following policies for receipt of samples:

1. Samples for BOD, Turbidity, 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.

2. Coliform bacteria samples expected to meet the required six-hour holding time will not be accepted after 4:00 PM on normal Monday through Thursday workdays.

3. All tube coliform samples must be scheduled in advance by contacting the laboratory.

The Washington Regional laboratory has established the following policies for receipt of samples:

1. Samples for BOD, Turbidity, 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.

2. Coliform bacteria samples expected to meet the required six-hour holding time will not be accepted after 4:00 PM on normal Monday through Thursday workdays.

Figure 6.1 Required Containers, Preservation Techniques and Holding Times (Water Quality Samples)

COLLECTION AND PRESERVATION OF **WATER QUALITY** SAMPLES FOR THE NC DWQ LABORATORY 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. The parameters are listed in the same order as they appear on the DM-1 form.

Samples must be shipped to the Laboratory as soon as possible after collection.

Parameter [1]	Minimum Required Volume	Container [14] P-Plastic G-Glass	Preservation[25]	Maximum Holding Time[26]
A. BOD 5-day	1 liter	P	Cool, 4°C	48 hours[2]
COD[19]	200 ml	P	Cool, 4°C, 25% H_2SO_4 to pH<2	28 days
Coliform (Total,Fecal, E.coli and Enterococci)	250 ml **each**	P[3] (sterile)	Cool, 4°C, 0.008% $Na_2S_2O_3$[3]	6 hours[4]
Residue[19] (TSS, TDS, TS)	500 ml **each**	P	Cool, 4°C	7 days
A. pH[5]	Inappropriate for laboratory analysis.			Immediate – field measurement
A. Acidity[19]	200 ml	P	Cool, 4°C	14 days
A. Alkalinity[19]	200 ml	P	Cool, 4°C	14 days
TOC	200 ml	P	Cool, 4°C, conc. H_3PO_4 to pH<2	28 days
Turbidity	200 ml	P	Cool, 4°C	48 hours[2]
Chloride	200 ml	P	None required	28 days
Chlorophyll *a*[11]	500 ml	P (Brown)	14 days in dark[13] Cool, 4°C	14 days[13]
Color	200 ml	P	Cool, 4°C	48 hours[2]
Chromium, Hexavalent	200 ml	P (Disposable)	Cool, 4°C	24 hours
Cyanide, Total	2 liters (two 1 liter bottles)	P	Cool, 4°C, 0.6g ascorbic acid[6] 6N NaOH to pH>12	14 days[23]
Fluoride	500 ml	P	None required	28 days
Formaldehyde	500 ml	P (Disposable)	Cool, 4°C	NA
Oil & Grease	2 liters (two 1 liter bottles)[18]	G (Wide mouth quart jar, Teflon-lined cap)	Cool, 4°C, 1:1 H_2SO_4 to pH<2	28 days
Hardness, Total (Request by checking Ca and Mg on fieldsheet - can be included as part of metals sample)[27]	500 ml	P (Disposable)	1+1 HNO_3 to pH<2	6 months
MBAS	500 ml	P	Cool, 4°C	48 hours[2]
Phenols	2 liters (two 1 liter bottles)	G (Phenol Bottle) only	Cool, 4°C, 1:1 H_2SO_4 to pH <2 (1 ml FAS if sample contains oxidizer)	28 days
Sulfate	500 ml	P	Cool, 4°C	28 days
Sulfide	500 ml [10]	P	Cool, 4°C, add 1 ml of 2N zinc acetate plus 6N NaOH to pH>9, no headspace.	7 days
Specific Conductance	200 ml	P	Cool, 4°C	28 days
B. NH_3 as N	500 ml x 1	P(Disposable)	Cool, 4°C, 25% H_2SO_4 to pH<2[7] 0.008%$Na_2S_2O_3$ [12]	28 days
B. TKN as N	Combined with above	P(Disposable)	Cool, 4°C, 25% H_2SO_4 to pH<2[7] 0.008%$Na_2S_2O_3$ [12]	28 days
B. NO_2 + NO_3 as N	Combined with above	P(Disposable)	Cool, 4°C, 25% H_2SO_4 to pH<2[7]	28 days
B. P, Total as P	Combined with above	P(Disposable)	Cool, 4°C, 25% H_2SO_4 to pH<2[7]	28 days
P, Dissolved as P	200 ml	P(Disposable)	Filter immediately; Cool, 4°C, 25% H_2SO_4 to pH<2[7]	28 days
PO_4 as P	200 ml	P(Disposable)	Filter immediately; Cool, 4°C	48 hours[2]

C. Metals[24]: Ag , Al, As, Be, Ba, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sn, Se, Tl, V, Zn and Hg	500 ml x 1	P(Disposable)	1+1 HNO_3 to pH<2	6 months. (**28 days for Mercury**)
Semi Volatile Organics (B/NA extractables)	1 gal	G (amber), Teflon-lined cap	Cool, 4°C, 0.008%$Na_2S_2O_3$[12]	7 days until extraction[8] 40 days after extraction
Pesticides/PCB's (OP pest/ OCl pest/ON pest)	1 gal	G (amber), Teflon-lined cap	Cool, 4°C, 0.008%$Na_2S_2O_3$[12]	7 days until extraction[8] [16], 40 days after extraction
Acid Herbicides	1 gal	G (amber), Teflon-lined cap	Cool, 4°C, 0.008%$Na_2S_2O_3$[12]	7 days until extraction[8] [16], 40 days after extraction
Purgeable Organics (VOA)	40 ml x 3 [10]	G, Teflon-lined septum	Cool, 4°C, 0.6g Ascorbic Acid [12][13] Sodium Bisulfate ($NaHSO_4$) to pH<2 [13] [15][17]	14 days (7 days when sample is unpreserved and aromatics only requested)
TPH - GRO and BTEX (aq)	40 ml x 3 [10]	G, Teflon-lined septum	Cool, 4°C, 0.6g Ascorbic Acid [12][13] Sodium Bisulfate ($NaHSO_4$) to pH<2 [13] [15][17]	14 days
TPH - DRO (aq)	1 gal	G, Teflon-lined cap	Cool, 4°C	14 days, analyze extract within 40 days

SOIL SAMPLES

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

Adopted from Tables 3-1 and 4-1 in *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition, 1986 and First Update in 1987.

Parameter/Analytical Group [1]	Minimum Required Volume	Container [14] P-Plastic G-Glass	(F) Filtered (U) Unfiltered	Preservation [25]	Maximum Holding Time[26]
Wet Chemistry analyses[20]	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	refer to aqueous
Nutrient analyses[21]	8 oz jar	G	N/A	Cool, 4°C	refer to aqueous
Micro analyses[22]	8 oz jar	G	N/A	Cool, 4°C	refer to aqueous
Metals analysis	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	refer to aqueous
Pesticides/PCB's (OP/OCl/ONpesticides)	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; analyze w/in 40 days
Acid Herbicides	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; analyze w/in 40 days
Semi Volatile Organics (B/NA extractables)	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; analyze w/in 40 days
Purgeable Organics (SVOA)	4 oz jar	G, Teflon-lined cap or septum	N/A	Cool, 4°C	14 days
TPH Gas Range (soil)	4 oz jar	G, Teflon-lined cap or septum	N/A	Cool, 4°C	14 days
TPH Diesel Range (soil)	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; Analyze w/in 40 days

Footnotes:

(1)Determinations preceded by the same letter may be submitted in the same bottle if the bottle contains enough sample. If no letter precedes a parameter, it must be submitted in a separate bottle (i.e. A, B, C).

(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.

(4)Litigation samples should be delivered to the laboratory within 5 hours of sample collection.

(5)It is recommended that pH analysis be performed on site. “Immediately” is defined as within fifteen minutes after collection.

(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 dropwise with stirring until the pH is lowered to <2.

(8)In a glass container, submit a small quantity of the pure compound of any suspected material.

(9)If residual chlorine is present, add 0.008% sodium thiosulfate dropwise to just neutralize the chlorine.

(10)Fill the bottle to overflowing and cap, leaving no air space.

(11)EPA Method 445.0, Revision 1.2, September 1997.

(12)Should only be used in the presence of residual chlorine. Add sodium thiosulfate or ascorbic acid (as directed) to the container first; fill at least half way before adding acid.

(13)Used by the DWQ 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.

(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)The entire contents must be used for analysis.

(19)COD, TS, TSS, Alkalinity and Acidity samples are to be shipped to the Central laboratory. They will then be repacked and routed to the Washington Regional laboratory for analysis. Samples collected in the Washington Region are sent directly to the Washington regional laboratory.

(20)Wet chemistry parameters include: Chloride, Chlorophyll *a*, Color, Hexavalent Chromium, Total Cyanide, Fluoride, Formaldehyde, Grease & Oils, MBAS, Phenols, Sulfate, Sulfide, Specific Conductance, and TDS.

(21)Nutrient parameters include: Ammonia Nitrogen, TKN, Nitrate+Nitrite Nitrogen, Total Phosphorous, Dissolved Phosphorous and Orthophosphate.

(22)Microbiology parameters include: BOD 5-day, Coliform (Total, Fecal, E. coli and Enterococci), Residue, pH, Acidity, Alkalinity, TOC, and Turbidity.

(23)Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be spot tested 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 $CdNO_3$ powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH>12.

(24)For dissolved metals, samples should be filtered immediately on-site before adding preservative.

(25)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 4°C until compositing and sample splitting is completed.

(26)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. Sample collectors must allow for preparation and analytical start-up. 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 which shows this is necessary to maintain sample stability.

(27)Total Hardness = 2.497[Ca] + 4.118 [Mg].

Figure 6.2 Required Containers, Preservation Techniques and Holding Times (Groundwater Samples)

COLLECTION AND PRESERVATION OF **GROUNDWATER** SAMPLES FOR THE NC DWQ LABORATORY SECTION

Listed below is information to be used in the collection and preservation of samples. Filtered samples are requested for some parameters as recommended by the USGS manual. **If you are submitting filtered samples, write "DIS" (for dissolved) in the block beside applicable parameters on the GS-54 form. Excluding purgeable organics and sulfide**, a one-half inch air space should be left in all bottles to allow for mixing before analysis. The parameters have been grouped according to preservatives needed. **Samples must be shipped to the Laboratory as soon as possible after collection.**

Parameter [2]	Minimum Required Volume	Container [1][14] P-Plastic G-Glass	(F) Filtered (U) Unfiltered	Preservation[22]	Maximum Holding Time[23]
A. Alkalinity[18]	200 ml	P	U	Cool, 4°C	14 days
A. Carbonate	Request on fieldsheet and submit Alkalinity sample.				6 months
A. Bicarbonate	Request on fieldsheet and submit Alkalinity sample.				6 months
A. pH	Inappropriate for laboratory analysis.				Immediate - field measurement
A. Carbon Dioxide	Inappropriate for laboratory analysis.				Immediate - field measurement
Chromium, hexavalent	200 ml	P	U	Cool, 4°C	24 hours
Color	200 ml	P	U	Cool, 4°C	48 hours[6]
MBAS	500 ml	P	U	Cool, 4°C	48 hours[6]
Specific Conductance	200 ml	P	U	Cool, 4°C	28 days
Chloride	200 ml	P	U	None required	28 days
Fluoride	500 ml	P	U	None required	28 days
Hardness, Total (Request by checking Ca and Mg on fieldsheet - can be part of metals sample) Total Hardness = 2.497[Ca]+4.118[Mg]	500 ml	P	U	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
Hardness, Non-carbonate[3]	Submit samples for Total Hardness (Ca+Mg) and Alkalinity as specified.				6 months
Oil & Grease	2 liters (two 1 liter bottles)	G (wide-mouth quart jar, Teflon-lined cap)	U	Cool, 4°C, 1:1 H_2SO_4 to pH<2	28 days
Silica	200 ml	P	U	Cool, 4°C	28 days
Sulfate	200 ml	P	U	Cool, 4°C	28 days
Cyanide	2 liters (two 1 liter bottles)	P	U	Cool, 4°C, 0.6g ascorbic acid[4], 6N NaOH to pH>12	14 days[12]
Phenol	2 liters (two 1 liter bottles)	G only	U	Cool, 4°C, 1:1 H_2SO_4 to pH<2 (1 ml FAS is sample contains oxidizer)	28 days
B. *Metals:* Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, Li, K, Mg, Mn, Na, Ni, Pb, Sb, Sn, Se, Tl, V, Zn and Hg	500 ml	P (Disposable)	U	1+1 HNO_3 to pH<2	72 hours (**should be delivered to lab within 48 hours to allow for sample prep**.) 28 days - Hg
BOD	1 liter	P	U	Cool, 4°C	48 hours[6]
COD[18]	200 ml	P	U	Cool, 4°C, 25% H_2SO_4 to pH<2	28 days
Coliform (Fecal or Total)	250 ml **each**	P (sterile)[7]	U	Cool, 4°C, 0.008% $Na_2S_2O_3$[7]	6 hours
TOC	200 ml	P	U	Cool, 4°C, H_3PO_4 to pH<2	28 days
Turbidity	200 ml	P	U	Cool, 4°C	To lab in <48 hours[6]
C. NH_3 as N	500 ml	P (Disposable)	U	Cool, 4°C, 25% H_2SO_4 to pH<2[11]	28 days
C. TKN as N	Combined w/ above	P (Disposable)	U	Cool, 4°C, 25% H_2SO_4 to pH<2[11]	28 days
C. NO_3 + NO_2 as N	Combined w/ above	P (Disposable)	U	Cool, 4°C, 25% H_2SO_4 to pH<2[11]	28 days
C. Total Phosphorous as P	Combined w/	P	U	Cool, 4°C, 25%	28 days

	above	(Disposable)		H_2SO_4 to pH<2[11]	
Dissolved Phosphorous as P	200 ml	P (Disposable)	F	Cool, 4°C, 25% H_2SO_4 to pH<2[11]	28 days
Orthophosphate as P	200 ml	P (Disposable)	F	Filter immediately, Cool, 4°C	48 hours[6]
Residue (TSS, TDS, TS)[18]	500 ml **each**	P	U	Cool, 4°C	7 days
Semi Volatile Organics (B/NA extractables)	1 gal	G (amber), Teflon-lined cap	U	Cool, 4˚C	7 days until extraction 40 days after extraction
Pesticides/PCB's (OP/OCl/ON pest)	1 gal	G (amber), Teflon-lined cap	U	Cool, 4˚C	7 days until extraction[16], 40 days after extraction
Acid Herbicides	1 gal	G (amber), Teflon-lined cap	U	Cool, 4°C	7 days until extraction[16], 40 days after extraction
Purgeable Organics(VOA)	40 ml x 3	G, Teflon-lined septum	U	Cool, 4˚C, 0.6g ascorbic acid only if residual chlorine present, Sodium Bisulfate ($NaHSO_4$) to pH2 [13] [15][17] No headspace.	14 days (7days when unpreserved sample submitted for aromatics only)
TPH Gasoline Range (aq) and BTEX	40 ml x 3	G, Teflon-lined septum	U	Cool, 4˚C, 0.6g ascorbic acid only if residual chlorine present, Sodium Bisulfate ($NaHSO_4$) to pH2 [13] [15][17] No headspace.	14 days
TPH Diesel Range (aq)	1 gal	G (amber), Teflon-lined cap	U	Cool, 4°C	14 days; analyze extract within 40 days

SOIL SAMPLES

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

Adopted from Tables 3-1 and 4-1 in *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition, 1986 and First Update in 1987.

Parameter [2]	Minimum Required Volume	Container [14] P-Plastic G-Glass	(F) Filtered (U) Unfiltered	Preservation [22]	Maximum Holding Time[23]
Wet Chemistry analyses[20]	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	refer to aqueous
Nutrient analyses[21]	8 oz jar	G	N/A	Cool, 4°C	refer to aqueous
Micro analyses[22]	8 oz jar	G	N/A	Cool, 4°C	refer to aqueous
Metals analysis	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	refer to aqueous
Pesticides/PCB's (OP/OCl/ON pest)	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; analyze w/in 40 days
Acid Herbicides	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; analyze w/in 40 days
Semi Volatile Organics (B/NA extractables)	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; analyze w/in 40 days
Purgeable Organics(VOA)	4 oz jar	G, Teflon-lined cap or septum	N/A	Cool, 4°C	14 days
TPH Gas Range (soil)	4 oz jar	G, Teflon-lined cap or septum	N/A	Cool, 4°C	14 days
TPH Diesel Range (soil)	8 oz jar	G, Teflon-lined cap	N/A	Cool, 4°C	14 days to extract; Analyze w/in 40 days
Purgeable Organics (5035) High-level	EnCore Sampler x 2		N/A	Cool, 4°C	48 hours to extrusion into MeOH

References:

Analytical Procedures, Appendix D Leaking Underground Fuel Tank Field Manual: Guidelines for Site Assessment, Clean-up and Underground Storage Tank Closure; State of California State Water Resources Control Board, Sacramento, Ca., October 1989.

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. The Branch Supervisor must approve methods from any other source.

Footnotes:
(1)P-Plastic, G- Glass, P(Disposable) - Plastic disposable bottle.

(2)Parameters preceded by the same letter may be submitted in the same bottle if the bottle contains enough sample. If no letter precedes a parameter, it must be submitted in a separate 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.

(8)Litigation samples should be delivered to the laboratory within 5 hours of sample collection.

(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.

(10)In a glass container, submit a small quantity of the pure compound of any suspected material.

(11)If residual chlorine is present, add 0.008% sodium thiosulfate dropwise to just neutralize the chlorine.

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

(13)Used by the DWQ 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)COD, TS, TSS, Alkalinity and Acidity samples are to be shipped directly to the Washington Regional Office for analysis. Samples collected in the Washington Region are sent directly to the Washington regional laboratory.

(19)Wet chemistry parameters include: pH, Acidity, Alkalinity, Chloride, Chlorophyll a, Color, Hexavalent Chromium, Total Cyanide, Fluoride, Formaldehyde, Grease & Oils, MBAS, Phenols, Sulfate, Sulfide, Specific Conductance, and TDS.

(20)Nutrient parameters include: Ammonia Nitrogen, TKN, Nitrate+Nitrite Nitrogen, Total Phosphorous, Dissolved P and Orthophosphate.

(21)Microbiology parameters include: BOD 5-day, Coliform (Total, Fecal, E. coli and Enterococci), Residue, TOC, and Turbidity.

(22) 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 4°C until compositing and sample splitting is completed.

(23) 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. Sample collectors must allow for preparation and analytical start-up. 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 which shows this is necessary to maintain sample stability.

7.0 Sample Custody and Handling

Many of the errors 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 procedures for the transportation, receipt, handling, protection, storage, retention and/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 Laboratory Section personnel and its clients in the *Sample Submission Guidance* document. This document is available for viewing on the Laboratory Section website at http://www.esb.enr.state.nc.us/lab/qa/sampsubguide.htm.

- 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 at the DWQ Laboratory Section 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 Laboratory Section follows both routine and legal chain-of-custody (COC) procedures, depending on the requirements of the client submitting the samples. The DWQ Laboratory 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 Laboratory Section 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 the field personnel must complete documentation of field collection, including the pertinent data on sample labels/tags and applicable fieldsheets. Samples are packed so that they are segregated by site, sampling location, sample analysis type, sample priority or by final destination.

A sample transmittal form (also referred to as a fieldsheet) must accompany all samples that are submitted to the Laboratory 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. An example fieldsheet supplied by the Central Laboratory is given in Figure 7.1 (Water Quality Section fieldsheet). The minimum information required on these records include:

(a) a unique (for that date/time/collector) sample location/field ID combination.
(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 and custody 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 are to be initiated by the sample collector and 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 errors shall be made by one line marked through the error. The individual making the correction shall sign or initial and date the correction.

An example COC form is given in Figure 7.2 (Water Quality Section COC). 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 technicians at the Regional Laboratories and the Support Unit personnel at the Central Laboratory are responsible for receiving samples shipped from or delivered by field personnel that collect water, soil or tissue samples throughout the state. Laboratory staff receive deliveries of all samples and initiate the first in-house records for a sample. When samples arrive at the laboratory, staff 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 filed in the sample folder. A copy of this form is sent with the final report to the collector.

7.3.1 Procedure

Laboratory staff 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 include 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 and/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 volatile samples (e.g., sulfide) are also inspected for headspace by chemists in the Volatile Organics analytical unit.

(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 prior to sample preparation or analysis in the analytical units after login and distribution and the process is documented on appropriate logs or laboratory bench worksheets.

At the time of receipt, laboratory staff check the temperature of the samples by measuring the temperature of the temperature blank. 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. Samples shall be deemed acceptable if arrival temperature is either within 0.1 to 6°C (with no evidence of freezing) 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 are generally discontinued at this point. Carrier, freight bill or other tracking numbers in shipping documentation are recorded on and/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 shall either:

- Retain all correspondence and/or records of communications with the sampler regarding the disposition of rejected samples, or

- 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.

- 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.

The custodian then assigns a chronological lab number 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 XWYYYY or XGYYYY where X is the number denoting the year, then either W (representing Water Quality) or G (representing Ground Water) 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 staff 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.

Copies of the fieldsheets are routed through applicable analytical units and the originals are sent to a Processing Assistant for entry into the laboratory data management system. All samples received by the Laboratory Section are logged into the Sample Tracking and Reporting Laboratory Information Management System (DWQ STAR LIMS) to allow the laboratory to track and evaluate sample progress.

The samples are logged into the DWQ STAR LIMS with the following information.

(a) lab number
(b) sample location/id/description
(c) mode of sample delivery (e.g. common carrier, Federal Express, etc.) and date
(d) lab comments
(e) date and time collected
(f) date and time received
(g) sample type
(h) sample priority
(i) analyses requested
(j) initials of the log-in person
(k) matrix

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.

After all the sample information is logged into the system, the sample is authorized in the DWQ STAR LIMS. The corresponding 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 Branch Managers and Unit Supervisors, 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 DWQ STAR LIMS and given a unique lab number. It is the responsibility of the Supervisor for each analytical unit to review the incomplete worklist daily with the chemists/technicians and report any problems with scheduling to the Branch Manager. The Branch Manager 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, manpower and instrument issues are discussed on a unit by unit basis and resolved. The Branch Manager tracks analytical units with limited capacity or scheduling issues and passes this information to the Section Chief 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. 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) temperature-controlled 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: VOA sample secondary aliquots
(f) VOA lab refrigerator #2: VOA aqueous and sediment samples
(g) lab freezer (G113): tissues and other samples requiring freezing
(h) lab freezer (G066): filtered chlorophyll samples

The regional laboratories store 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 4°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. Samples may not be stored in the refrigerator compartment of a unit that has standards stored in the freezer compartment. Sample fractions, extracts, digestates, and other sample preparation products shall be stored according to Section 6.0 (or according to the specifications in the test method) in controlled storage areas in the analytical unit.

The Laboratory 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 DWQ Laboratory Section personnel only. Visitors to the laboratory are prohibited from entering the refrigerator and laboratory areas unless accompanied by an employee of the Laboratory 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, and/or sample submitter must participate in the decision about the sample's disposal.

Disposal is performed in accordance with local, state, and US EPA-approved methods. 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) The sample may be stored after analysis (samples are normally maintained no longer than 90 days from receipt unless otherwise requested and discarded when all laboratory analyses for that sample are complete.

7.7 Sample Custodians

Personnel working in the sample receiving room or sample receiving area are designated as sample custodians. The managers, 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 Laboratory 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 delivered to the receiving lab with the associated samples. The delivery technician and the recipient at the receiving lab must sign the COC indicating the transfer dates and times.

7.9 Sample Tracking and Reporting Laboratory Information Management System (DWQ STAR LIMS)

The laboratory uses a customized Excel© based LIMS, which runs on a Windows© operating system over a Novell Netware© LAN. The main server and the applications and hardware are maintained by the Bio/Chemistry Unit Supervisor.

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

When all the analyses for a sample are complete and the sample is authorized for release, two copies of the report are printed. The Branch Managers 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 fieldsheets to the client. Clients may also access the report via the state's WAN.

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 and/or hardware is performed each time when any part of it is used. Any abnormalities are reported to the Bio/Chemistry Unit Supervisor immediately for quick corrective action(s).

Figure 7.1 Water Quality Section Fieldsheet.

DIVISION OF WATER QUALITY - LAB FORM

COUNTY : _____
RIVER BASIN : _____
REPORT TO : _____
SHIPPED BY : _____
COLLECTOR(S) : _____

PRIORITY
☐ AMBIENT ☐ QA
☐ COMPLIANCE ☐ CHAIN OF CUSTODY
☐ EMERGENCY

☐ W SAMPLE TYPE
☐ STREAM ☐ EFFLUENT
☐ LAKE ☐ INFLUENT
☐ ESTUARY

Lab Number : _____
Date Received : _____
Time Received : _____
Received By : _____
Data Released : _____
Date Reported : _____

Estimated BOD Range: Station Location: _____
Seed: _____ Chlorinated: _____ Remarks: _____

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

	BOD 310	mg/L		Chloride 940	mg/L		NH3 as N 610	mg/L		Li- Lithium 1132	ug/L
	COD High 340	mg/L		Chl a: 70953	µg/L		TKN as N 625	mg/L		Mg- Magnesium 927	mg/L
	COD Low 335	mg/L					NO2 plus NO3 as N 630	mg/L		Mn- Manganese 1055	µg/L
	Coliform: MF Fecal 31616	#/100 mls					P: Total as P 665	mg/L		Na- Sodium 929	mg/L
	Coliform: MF Total 31504	#/100 mls		Color: True 80	c.u.		PO4 as P 70507	mg/L		As- Arsenic:Total 1002	µg/L
	Coliform: Tube Fecal 31615	#/100 mls		Color: (pH) 83 pH	c.u.		P: Dissolved as P 666	mg/L		Se- Selenium 1147	µg/L
	Coliform: Fecal Strep 31673	#/100 mls		Color: pH 7.6 82	c.u.		K- Potassium	mg/L		Hg- Mercury 71900	µg/L
	Residue: Total 500	mg/L		Cyanide 720	mg/L		Cd- Cadmium 1027	µg/L		Ba- Barium	µg/L
	Volatile 505	mg/L		Fluoride 951	mg/L		Cr- Chromium:Total 1034	µg/L		Organochlorine Pesticides	
	Fixed 510	mg/L		Formaldehyde 71880	mg/L		Cu- Copper 1042	µg/L		Organophosphorus Pesticides	
	Residue: Suspended 530	mg/L		Grease and Oils 556	mg/L		Ni- Nickel 1067	µg/L			
	Volatile 535	mg/L		Hardness Total 900	mg/L		Pb- Lead 1051	µg/L		Acid Herbicides	
	Fixed 540	mg/L		Specific Cond. 95	µmhos/cm2		Zn- Zinc 1092	µg/L			
	pH 403	units		MBAS 38260	mg/L		V- Vanadium	µg/L		Base/Neutral&Acid Extractable Organics	
	Acidity to pH 4.5 436	mg/L		Phenols 32730	µg/L		Ag- Silver 1077	µg/L		TPH Diesel Range	
	Acidity to pH 8.3 435	mg/L		Sulfate 945	mg/L		Al- Aluminum 1105	µg/L			
	Alkalinity to pH 8.3 415	mg/L		Sulfide 745	mg/L		Be- Beryllium 1012	µg/L		Purgeable Organics (VOA bottle req'd)	
	Alkalinity to pH 4.5 410	mg/L		Boron: Total 1022	µg/L		Ca- Calcium 916	mg/L		TPH Gasoline Range	
	TOC 680	mg/L		Tannin & Lignin 32240	µg/L		Co- Cobalt 1037	µg/L		TPH/BTEX Gasoline Range	
	Turbidity 82079	NTU		Hexavalent Chromium 1032	µg/L		Fe- Iron 1045	µg/L		Phytoplankton	
	Coliform Total Tube 31508	#/100 mls									

COMMENTS : _____

LAB USE ONLY
Temperature
on arrival (ºC):

Sample Point % (2)	Conductance (94)	Water Temp-C (10)	D.O. (300)	pH (400)	8.3 Alkalinity (82244)	4.5 Alkalinity (431)	4.5 Acidity (82243)	8.3 Acidity (82242)	Air Temp-C (20)
Secchi depth m	Salinity ppt (480)	Precipit-In/day (45)	Cloud Cover % (32)	Wind Dir-Deg (36)	Strm Flow Sev (1351)	Turbidity Severity (1350)	Wind Velocity-mph (3	Mean Strm Depth-ft (64)	Strm Width-ft (4)

Figure 7.2 Division of Solid Waste Management Chain of Custody Form

Report to: _____ DIVISION OF WASTE MANAGEMENT – WATER QUALITY SECTION (WQ) Page _____ of _____

CHAIN OF CUSTODY RECORD

NC DENR/DWQ LABORATORY (check one): [ ] CENTRAL [ ] ARO [ ] WaRO

For Investigation of:						**Incident No.**
Sample collector (print name) and DM-1 forms 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) and III (12/96); 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.

8.1.2 SM##

- APHA, AWWA, WEF. 1992. Standard Methods for the Examination of Water and Wastewater, 18th Edition (designated as SM18 in Table 5.1).
- APHA, AWWA, WEF. 1995. Standard Methods for the Examination of Water and Wastewater, 19th Edition (designated as SM19 in Table 5.1).
- APHA, AWWA, WEF. 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition (designated as SM20 in Table 5.1).

8.1.3 CA LUFT

- Leaking Underground Fuel Tank Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure, Method for Determination of Petroleum Range Organics October, 1989, State of California Leaking Underground Fuel Tank Task Force (designated CA LUFT).

8.1.4 Other Reference Procedures

Other reference procedures for non-routine analyses may include methods established by a specific state (e.g., MA DEP EPH) 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. The Laboratory Section has modified some of these methods 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 study and are closely monitored for precision and accuracy. 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 have been made to methods indicated in Table 5.1:

8.2.1 EPA 200.2

Method 200.2 (hot plate) is modified and validated for use with a block digestor. 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

Standard Methods 5220 D allows the use of alternative digestion vessels and reagents (see Standard Methods 5220 D 2 (a) and 5220 C 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.

8.3 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 SM18 3030C

This method is for digesting Groundwater Section's water samples per memoranda, "Policy on Treatment of Groundwater Samples for Metals Determinations Required by 15A NCAC 2L", January 26, 1993, Arthur Mouberry, Groundwater Section Chief and "Request to Change Groundwater Section's Metals Policy", October 25, 2001, Arthur Mouberry, Groundwater Section Chief. The effective date for this method was March 1, 1993. A copy of this document is included in Figure 8-1.

8.3.3 EPA 200.2

U.S. EPA Region 4 has provided written approval to the NC DWQ Laboratory Section for the use of EPA 200.2 for NPDES compliance monitoring. A copy of this document is included in Figure 8-2.

8.3.4 EPA 200.8

U.S. EPA Region 4 has provided written approval to the NC DWQ Laboratory Section for the use of EPA 200.8 for NPDES compliance monitoring. A copy of this document is included in Figure 8-3 and an electronic mail notice of clarification regarding this approval is included in Figure 8-4.

8.3.5 EPA 200.9

U.S. EPA Region 4 has provided written approval to the NC DWQ Laboratory Section for the use of EPA 200.9 on wastewater. A copy of this document is included in Figure 8-5.

8.3.6 Platinum-Cobalt Color (SM18 2120 B)

U.S. EPA Region 4 has provided written approval to the NC DWQ Laboratory Section for the use of a spectrophotometer operating at a wavelength of 460 nm in place of the visual comparison method for wastewater samples. Copies of the original request for approval and of EPA's responses are included in Figures 8-6 and 8-7, respectively.

8.3.7 Anions by Ion Chromatography (EPA 300.0)

U.S. EPA Region 4 has provided written approval to the NC DWQ Laboratory Section for the use of EPA 300.0 on wastewater. PENDING

8.4 Standard Operating Procedures

The DWQ Laboratory Section has developed Standard Operating Procedures (SOPs) for all analytical procedures and laboratory operations. The method 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 and/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, practical quantitation limit, 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 Section Chief, Branch Managers and the QA/QC Coordinator. All SOPs are controlled in the laboratory: numbered sequentially, approved and signed by the unit Supervisor, the Branch Manager, and QA Officer, dated with an effective date, placed in controlled manuals or placed in a read-only format on the network, and archived when updated. Procedures for preparation, review, revision and control are incorporated by reference to SOP# QAG001. 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 Laboratory Section 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/CCV 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.

All demonstrations shall be documented through the use of the IDOC Certification Statement form in Figure 4-6.

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

a) A quality control sample shall be obtained from an outside source. 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.

b) The analyte(s) shall be diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified by a method, or if unspecified, to a concentration approximately 10 times the method-stated or laboratory-calculated method detection limit.

c) At least 4 aliquots shall be prepared and analyzed according to the test method either concurrently or over a period of days.

d) Using all of the results, 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 acceptance criteria for precision and accuracy in the test method (if applicable) or in 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.
- 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) 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.

h) 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, the dilution of samples and blank analysis. Reagent water should have no detectable concentration of the compound or element to be analyzed at the detection limit of the analytical method. Reagent water must be free of substances that interfere with analytical methods. Laboratory reagent water is generally prepared by passing tap water through a reverse osmosis system or a still and meets or exceeds ASTM Type II Reagent Grade Water requirements. It must have a resulting specific conductance of less than 2 μmhos/cm. The conductivity is checked and recorded monthly. If the water's specific conductance exceeds the specified limit, the analyst must immediately initiate corrective action. Non-chlorinated well water is used for organic analyses. For volatile organics analyses, this well water is also passed through an activated charcoal filter before use.

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 or are purchased from reputable vendors. Standards and reagents are prepared using balances in which the calibration is verified daily, Class A volumetric glassware or pipettors which are 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.

Material Safety Data Sheets (MSDS) are kept in a central location known to all personnel and each analytical unit shall have copies of MSDS for the chemicals used in that unit. Anyone may review these for relevant information on the safe handling and emergency precautions of chemicals used and stored on-site. 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. All 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, and 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 autopipette) 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 identity, analyst, titer or concentration, solvent (when applicable), preparation date 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. Storage requirements are generally described in the associated SOP. 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 upon expiration. When expiration dates are not specified, the following guidelines are used:

- Stock Standards used 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.

- Titrating solutions need to be either restandardized or a new bottle of vendor-certified standard opened each month. Titrating solutions used by the Laboratory Section include 0.02*N* sulfuric acid (alkalinity) and 0.025*N* sodium thiosulfate (BOD and total phenol), 0.0192*N* silver nitrate (cyanide), 0.1*N* HCl (formaldehyde), and 0.0141*N* silver nitrate (chloride).

- 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 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 preparation 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 time period of valid use of 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 Material 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. 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.

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 MSDS.

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 are stored in the dry chemical storage area of the chemical supply room. Organic and inorganic reagents are stored on separate shelves. Reactive chemicals are isolated from other materials. The dry chemical storage area is air-conditioned.

Light-sensitive reagents may be stored in amber/brown-glass containers. Specific storage instructions are detailed in the laboratory SOPs.

Organic extracts and stock solutions are stored in a freezer in the appropriate operational unit. Working solutions are refrigerated or frozen as appropriate. 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 Laboratory Section collects, stores, packages, labels, ships 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 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. The selection of the waste transporter 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 waste organic solvents in the laboratory include organic sample preparation and standard/reagent preparation. Laboratory wastes are stored in labeled four-liter or 2.5 liter glass bottles. These containers are stored closed in fume hoods in the appropriate analytical units. At the Central Laboratory, when the waste bottle is full, the contents are transferred into a 55-gallon drum labeled "Waste Flammable Liquid "in the waste storage room. Fifty-five gallon drums are maintained by the laboratory in compliance with RCRA regulations for disposal of waste solvents. All records of waste disposal are maintained. Records include waste disposal manifests, correspondence from disposal firms and any other information necessary to document the disposal of laboratory wastes. Organic solvents containing PCB's are segregated for 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.

Only completed samples (including raw samples, extracts, and digestates) with authorized reports (checked from DWQ STAR LIMS) are disposed. The Central Laboratory has a two-stage sewage system. Laboratory drains are separated from the sanitary drains. The laboratory room drains are collected and passed through a calcium carbonate filter to neutralize acids, and then are passed into the normal sanitary sewer system. The sanitary drains

bypass the pretreatment phase and drain directly to the sanitary sewer system. Non-hazardous, unpreserved aqueous samples are poured down the sink drain while flushing with tap water. Non-hazardous, preserved aqueous samples are neutralized with sodium bicarbonate and then poured down the sink drain 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. General procedures for cleaning laboratory glassware and other labware for specific applications are outlined in Table 8-1.

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, nitric acid should be replaced by hydrochloric acid, or hydrochloric acid may be used after the nitric acid rinse.
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).

8.9.3 Labware storage

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

Figure 8-1. Memorandum from the Groundwater Section implementing the use of Method 3030C for the preparation of Groundwater water samples.

Division of Water Quality

Groundwater Section

October 25, 2001

Memorandum

RECEIVED
OCT 29 2001
DWQ
LABORATORY SECTION

To: Steve Tedder
Chief, Laboratory Section

From: Arthur Mouberry
Chief, Groundwater Section

Subject: Request to Change Groundwater Section's Metals Policy

The Groundwater Section's current metals policy requires use of Standard Method 3030C, "Treatment for Acid-Extractable Metals," and applies to all groundwater samples collected for metals except mercury. This policy was adopted to address problems due to various amounts of sediment and turbidity in many groundwater samples and to ensure consistent treatment of samples by samplers and laboratories. Standard Method 3030C requires field acidification of unfiltered samples and acid extraction in the laboratory followed by filtration. Use of 0.45 micron filters and a 72-hour holding time from sample collection to filtration were specified as conditions.

In an effort to maximize use of laboratory staff time, the Division of Water Quality Chemistry Lab recently recommended changes to the Groundwater Section's 3030C metals preparation policy that would eliminate some low turbidity samples from the filtration requirement and allow a larger filter size for others. The Lab's recommendations, and other metals policy options, were presented at the Groundwater Section Supervisors' Meeting held October 17-19, 2001.

After reviewing the Lab's recommendations and other options, the Groundwater Section has decided to generally exclude water supply well samples from the 3030C metals preparation procedure requirement. Field staff will be reminded to check "water supply well" on sample tags and to list "water supply well" on field sheets when appropriate. Water supply well samples may be analyzed for "total metals," in accordance with Standard Method 3030A (Introduction to "Preliminary Treatment of Samples"), which will eliminate most of those samples from the digestion and/or filtration requirement due to low turbidity (<1 NTU). Water supply well samples with turbidity >1 NTU, and all monitor well samples must be run using the 3030C procedure. A few specific Groundwater Section investigations may involve a network of water supply wells and associated monitor wells. For such investigations, samplers may request both "total metals" analysis and the "3030C metals preparation" analysis for affected water supply wells, to ensure consistency in methodology when comparing monitor well/water supply well results.

The Groundwater Section decided to not make filter size changes to the 3030C metals preparation procedure at this time. Should there be a need to review the Groundwater Section's metals policy again, we would be happy to accept your offer to assist us with a study.

If you need additional information, please contact me at (919) 715-6170 or Betty Wilcox at (919) 715-6167.

cc: Regional Supervisors
Greg Thorpe
Ted Bush
Debra Watts
Larry Ausley
Roy Byrd
Dana Satterwhite
Betty Wilcox
Files

Figure 8-2. 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 8-3. EPA Region 4 approval for EPA Method 200.8.

2/Roy

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~~ Roy Byrd 11-8-2000. * 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.

*See E-mail attached
Roy Byrd 11-8-2000

Sincerely,

Russell L. Wright, Jr.
Director

cc: James Meyer, NC-DENR

Figure 8-4. 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 8-5. 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 1 6 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,

Gary Burnett /for

Allan E. Antley
Acting Director

cc: Mr. James Meyer, NC DEHNR

Figure 8-6. Request for approval 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

An Equal Opportunity Affirmative Action Employer

Figure 8-7. EPA Region IV 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 DWQ laboratories are equipped with state-of-the-art instrumentation. Major equipment lists for each of the laboratories are found in Tables 4-1, 4-2 and 4-3 of this document. Laboratory personnel routinely calibrate all instruments and equipment used within the Laboratory Section. Some instruments and/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*. 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 prepared 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 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.

- 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 PQL, but a standard is analyzed at the PQL concentration either as part of the curve or as a daily check. 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 diluted to fall within the range of calibration or be reported as having less certainty by means of defined qualifiers or case narratives (with the exception of ICP methods or other methods where the referenced method does not specify two or more standards).

- 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.

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 in the analytical units and periodically archived into a data storage area. Initial and continuing calibrations are sorted by date for ease of location. All assigned unique standard 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), 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 over which quantitation will occur. 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 0.995, b) the relative response factors (response factor/calibration value) over the range of calibration must have a relative standard deviation of less than or equal to 10% or c) 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-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.

Alternatively, software programs are used that calculate sample concentrations directly from the calibration curve.

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:

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

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:

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

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

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:

$$s^2 = \frac{[\text{The sum of } (x - \text{mean})^2]}{(n-1)}$$

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

RSD = (SD/mean CF) x 100
RSD = (SD/mean RF) x 100

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.

9.3.6 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 and/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.

9.3.7 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 and/or may cause unnecessary reanalysis of sample when surrogates or spiked compounds are erroneously not 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.

9.3.7.1 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.

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.

9.3.8 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 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). 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 non-detects, then those non-detects may be reported with the appropriate qualification. Otherwise, the samples affected by the unacceptable calibration verification shall 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 the appropriate 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.

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, e.g., the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the limit. 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.

9.3.9 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.

$$\% \text{ Difference} = \frac{CF(v) - \overline{CF}}{CF} \times 100 \quad \text{or} \quad = \frac{RF(v) - \overline{RF}}{RF} \times 100$$

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.

9.3.10 Verification of Non-Linear Calibrations

Calibration verification of a non-linear calibration is performed using the percent drift calculation described in Section 9.3.9. 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, then adjust the instrument operating

conditions and/or perform instrument maintenance, and analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, then a new initial calibration is performed.

All target analytes and surrogates, including those reported as non-detects, must be included in a periodic calibration for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met. The frequency 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 ±0.10 pH units of its given value. Manual or automatic temperature compensation is performed, depending on the meter. 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.

Calibration information from manual determinations is recorded in a calibration logbook for the pH meter and/or on laboratory bench worksheets.

Analytical Balance

Electronic analytical balances are calibrated daily with internal mechanisms, if available. The calibration of the balance must be checked daily by the analysis of two Class S (or equivalent) weights that bracket 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. 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.

Thermometer Calibration and Temperature Checks

Equipment such as refrigerators, freezers, ovens, waterbaths, hot blocks, and incubators are periodically checked with calibrated or 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 and waterbaths 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

thermometers are calibrated annually against an NIST-certified thermometer. Thermometers are replaced when they are not within allowable tolerances, otherwise they are labeled and the proper correction is applied.

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 (CCV) standard 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 Continuing Calibration Verification (CCV) Standard 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 CCV 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
Interference Check Solutions	±20% of true value
Continuing Calibration Verification (CCV)	±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:

- Ba^{++}/Ba^{+} 69 ratio is ≤ 3 %;
- CeO^{+}/Ce^{+} 155.9 ratio is ≤ 3 %;
- Mg 4 intensity must be ≥ 20,000 ions/sec:
- In 114.9 intensity must be ≥ 300,000 ions/sec;
- Rh 102.9 intensity must be ≥ 150,000 ions/sec.
- Pb 208.0 intensity must be ≥ 100,000 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 four 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 90-110 %.
- 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 10% 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 floppy disk and to the network, where it is stored permanently on optical disk.

ICP-MS (Elan 6100) Calibration Protocol Summary.

Calibration Check	**200.8 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 (CCV)	±10% 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 correlation coefficient of the regression curve must be greater than or equal to 0.995. An initial calibration verification (ICV) standard is analyzed immediately upon calibration and must meet acceptance criteria. Continuing calibration verification (CCV) standards are analyzed after every 10 samples and at the end of the sequence and must meet the acceptance criteria. A calibration blank (ICB or 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 (CCV)	±10% of true value	+10% of true value
Continuing Calibration Blank (CCB)	<½PQL	<½PQL

All sample results must be bracketed by acceptable calibration standards.

FLAA (Flame Atomic Absorption) Calibration Protocol Summary.

Calibration Check	**200 series**
Minimum number of calibration points	4
Initial Calibration Verification (ICV)	±10% of true value
Initial Calibration Blank (ICB)	<½PQL
Continuing Calibration Verification (CCV)	±10% of true value
Continuing Calibration Blank (CCB)	<½PQL

All sample results must be bracketed by acceptable calibration standards.

CVAA (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 (CCV)	±10% of true value
Continuing Calibration Blank (CCB)	<½PQL

All sample results must be bracketed by acceptable calibration standards.

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 20 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. 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) of -1.00 ±0.08.
- 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 Continuing Calibration Check Standard (CCCS) 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.

ISE 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 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 (CCV) standards are analyzed at the concentration mid-point of the initial calibration. The CCV are analyzed every 10 samples, to insure the continuing validity of the initial calibration. The CCV 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 Cal/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 (CCV) 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 three samples in the case of sulfate turbidimetric 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 every three years according to 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 is 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 (except for the 14.9 µmhos/cm standard, which must be ±20% of the known value). For meters not having automatic temperature compensation, samples are either analyzed at 25°C ±2 °C or a manual temperature correction is employed.

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 three protocols: EPA 600 series, EPA 8000 series and the State of California Leaking Underground Fuel Tank Field Manual (CA LUFT-TPH). These analyses are generally performed using external standard calibration and quantitation; therefore the absolute retention time is used to determine the identification of the target compounds. The 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 CCV will be required for external standard calibrations as specified in the method or SOP. If internal standard calibration and quantitation is used, the relative retention time, as defined in the respective SOPs, will be used to determine the identification of the target compounds and bracketing by CCV will not be required unless specified in the method.

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 either internal standard or external 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. An alternative to quantitation from a calibration curve is quantitation from an average calibration factor or average response factor. If the %RSD is less than or equal to the acceptance criteria, the average response factor can be used for quantitation.

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.

Calibration Check	600 series	8000 series	CA LUFT - TPH GRO
Initial calibration	Minimum of 3 standards	Minimum of 5 standards	Minimum of 3 standards
%RSD criteria (1)	RF≤10%	CF or RF≤20%	N/A
CCV criteria (%difference or %drift)	Within Q-table values	±15%	±10%
Frequency of CCV	Daily	Every 12 hours	Daily

(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 CCV - Samples analyzed by external standard calibration require bracketing by CCV. If the CCV standard 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 RL may be reported as <RL, since the compounds would have been detected if present. (SW-846 Method 8000 B).

Semivolatiles by GC

Semivolatile organic compounds (SVOCs) are analyzed by four protocols: EPA 500 series, EPA 600 series, EPA 8000 series and the State of California Leaking Underground Fuel Tank Field Manual (CA LUFT - TPH). If internal standard calibration is used; relative retention time, as defined in the respective SOPs, will be used to determine the identification of the target compounds and bracketing by CCV 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 CCV 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 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 the internal standard or external 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. An alternative to quantitation from a calibration curve is quantitation from an average response factor. If the %RSD is less than or equal to the acceptance criteria, the average response factor can be used for quantitation.

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.

Calibration Check	500 series	600 series	8000 series	CA LUFT - TPH DRO
Initial calibration	Minimum of 3 standards (as the calibration range is extended, the number of points must be increased)	Minimum of 3 standards	Minimum of 5 standards	Minimum of 3 standards

%RSD criteria (1)	RF≤20%	RF≤10%	CF or RF≤20%	N/A
CCV criteria (%difference or %drift)	±20%	±15% (non-40 CFR Methods are ±10%)	±15%	±10%
Frequency of CCV	Every 8 hours	Daily	Every 12 hours	Daily

(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 CCV - Samples analyzed by external standard calibration require bracketing by CCV. If the CCV standard 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 RL may be reported as <RL, since the compounds would have been detected if present. (SW-846 Method 8000 B).

9.4.5 Gas Chromatography/Mass Spectrometry (GC/MS)

Volatiles by GC/MS

Volatile organic compounds (VOCs) are analyzed by two protocols: 600 series and 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 VOC tuning with 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 the 600 series and every 12 hours for the 8000 series. The tune analysis must meet the criteria listed in EPA methods 624 and 8260 for a 25-ng injection of bromofluorobenzene (BFB).

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (BFB)		
Ion Abundance Criteria		
m/e	**624**	**8260**
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 600 series and a minimum of 5 levels is required for the 8000 series.

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. An alternative to quantitation from a calibration curve is quantitation from an average response factor. If the %RSD is less than or equal to the acceptance criteria, the average response factor can be used for quantitation.

A mid-level calibration verification standard must be analyzed periodically (daily for 600 series and every 12 hours for the 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/MS		
Method	**Initial Calibration Check Criteria**	**Continuing Calibration Check Criteria**
624	All targets ≤35% RSD, or alternatively, construct calibration curve.	QC Check Sample (20 µg/L) meets limits specified in method - Table 5, Range for Q
8260	CCC ≤30% RSD Target analytes <15% RSD	CCC ≤20% difference or drift from initial calibration
	SPCC (minimum 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 criteria is adopted from the EPA CLP Low Level Statement of Work, a protocol similar in scope and application to SW-846 Method 8260.

A Quality Control Check Standard (QCCS) 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 QCCS is analyzed every time the instrument is calibrated and during every 12 or 24 hour analytical shift. The QCCS 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 8260 - After the CCC and SPCC are evaluated, all target compounds are evaluated for linearity. If the %RSD is less than or equal to 15%, the average response factor can be used for quantitation. If the %RSD exceeds 15%, 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 QCCS, 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 tape or optical disk for permanent storage.

Semivolatiles by GC-MS

Semivolatile compounds are analyzed by two protocols: 600 series and 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 decafluorotriphenyl phosphine (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 600 series and every 12 hours for 8000 series.

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (DFTPP)		
Ion Abundance Criteria		
m/e	**625**	**8270**
51	30-60% of mass 198	30-60% 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 60
127	40-60% of mass 198	40-60% of mass 198
197	<1% of mass 198	<1% of mass 198
198	Base peak, 100% relative abundance	Base peak, 100% relative abundance
199	5-9% of mass 198	5-9% of mass 198
275	10-30% of mass 198	10-30% of mass 198
365	>1% of mass 198	>1% of mass 198
441	Present but less than mass 443	Present but less than mass 443
442	>40% of mass 198	>40% of mass 198
443	17-23% of mass 442	17-23% 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. The correlation coefficient of the calibration curve must be greater than or equal to 0.99. An alternative to quantitation from a calibration curve is quantitation from an average response factor. If the %RSD is less than or equal to the acceptance criteria, the average response factor can be used for quantitation.

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.

Semivolatile GC/MS		
Method	**Initial Calibration Check Criteria**	**Continuing Calibration Check Criteria**
625	All targets ≤35% RSD, or alternatively, construct calibration curve.	All targets ≤20% difference from initial calibration.
8270	CCCs ≤30% RSD; RF of SPCCs ≥0.050	RF of CCCs ≤20% difference or drift from initial calibration; RF of SPCCs ≥0.050

SW-846 Method 8270 - After the CCC and SPCC are evaluated, all target compounds are evaluated for linearity. If the %RSD is less than or equal to 15%, the average response factor can be used for quantitation. 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 sec. from the last CCCS, 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 CCCS, 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.

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. The term “independent source” means that the origins 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 with the initial calibration data file name. All raw electronic data files are initially stored on the MS system hard disk, then later archived to RW CD for permanent storage.

9.5 Standardization of titrating solutions

The titrants for all titrametric 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	Class S or equivalent weights	ASTM tolerances
	Quarterly	3 point verification	Class S or equivalent weights	ASTM tolerances
Ovens	Daily	Temperature checked and recorded	NIST traceable thermometer	Varies according to use - see determinative SOP
Incubators	Twice Daily	Temperature checked and recorded	NIST traceable thermometer	Varies according to use - see determinative SOP
Autoclaves	Daily	Maximum temperature and pressure recorded	NIST traceable thermometer and pressure gauge	Varies according to use - see determinative SOP
Water baths	Daily	Temperature checked and recorded	NIST traceable thermometer	Varies according to use - see determinative SOP
Refrigerators	Daily	Temperature checked and recorded	NIST traceable thermometer	1 to 6°C with no evidence of freezing
Freezers	Daily	Temperature checked and recorded	NIST traceable thermometer	-10°C to - 20°C
Thermometers, Hg or spirit-filled	Annually	Verified against an NIST or NIST traceable thermometer	NIST traceable thermometer	Varies according to use - see thermometer calibration SOP
Thermometers, Digital	Quarterly	Verified against an NIST or NIST traceable thermometer	NIST traceable thermometer	Varies according to use - see thermometer calibration SOP
Pipettors	Quarterly	Verified gravimetrically	Class S or equivalent weights	±1% 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) ***ICP spectrophotometer***	Daily or failure of CCV	Calibration (4-6 points)	Vendor certified standard. Plasma grade-ICP	Correlation coefficient >0.995
	Immediately following calibration, 10% and end of run	ICV/CCV	Mid-range calibrant	±5% immediately following calibration then ±10% of initial value after every 10 samples and at the end of the run.
	Daily following CCV and at end of run	Second source QC	Certified reference material	±10% of true value
Ion chromatograph	Daily or failure of ICV/CCV	Calibration (3-5 points)	Vendor certified standards	Correlation coefficient > 0.995
	Immediately following calibration and end of run.	CCV	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	CCV	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	Calibration (3 to 5 points)	Vendor certified standards	Correlation coefficient >0.995
	Annually	Calibration (5 points)	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%

Table 9-2. ***cont'd.***

GC Semivolatiles	Initially and every 12 or 24 hours	Injection port contamination check	DDT/Endrin	<15% degradation
	Initially or upon failure of CCC	Calibration (3 to 5 points)	Vendor certified standards	Coefficient of determination >0.990
	After initial calibration	Second source standard	Vendor certified standard	<20% difference
	Every 12 or 24 hours	CCC	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 or 24 hours	Instrument tune	DFTPP	Method specified criteria
	Initially, upon failure of CCC and every 12 or 24 hours	Calibration (3 to 5 points) SPCC CCC	Vendor certified standards	SPCC minimum RF 0.05 CCC ≤30% RSD
	After initial calibration and at end of batch	Second source QC	Vendor certified standard	≤30% difference
GC/MS Volatiles	Every 12 or 24 hours	Instrument tune	BFB	Method specified criteria
	Initially and upon failure of CCC	Calibration (3 to 5 points)	Vendor certified standard	Minimum RF 0.05
	After initial calibration and end of every 12 or 24 hour run	Second source QC	Vendor certified standard	≤30% difference from initial calibration
	Every 12 or 24 hours	CCC	50 ppb calibrant	<30% difference form initial calibration
	Every 12 or 24 hours	SPCC	50 ppb calibrant	Minimum RF 0.3
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 CCV	Calibration (4 points)	Vendor certified standard.	Correlation coefficient >0.995
	Immediately following calibration, 10% and end of run	ICV/CCV	Mid-range calibrant	±10% immediately following calibration then ±15% of initial value after every 10 samples and at the end of the run.
	Daily following CCV and at end of run.	Second source QC	Certified reference material	±10% of true value

Table 9-3. Standardization of Titrating Solutions.

Titrating Solution	Primary Standard	Source of Primary Standard	Frequency of Standardization
Sulfuric Acid	Sodium carbonate solution	Commercial supplier	Every 7 days.
EDTA	Calcium carbonate solution	Commercial supplier	Each day of use.
Sodium Thiosulfate	Potassium bi-iodate solution	Commercial supplier	Every month.
Mercuric Nitrate	Sodium chloride solution	Commercial supplier	Each day of use.
Silver Nitrate	Sodium chloride solution	Commercial supplier	Each day of use.
Cyanide Standard	Silver nitrate solution	Commercial supplier	Each day of use.
Ferrous Ammonium Sulfate (FAS)	Potassium Dichromate Solution	Prepared in lab from reagent grade source	Each day of use.
Formaldehyde	0.1N HCl	Prepared and standardized in lab from reagent grade source	Every 6 months.
Phenol	0.025N Sodium Thiosulfate	Prepared and standardized in lab from reagent grade source	Each day of use.

10.0 Preventive Maintenance

The Central Laboratory is equipped with 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 shall be kept for all major pieces of equipment. It is the responsibility of each Unit Supervisor to ensure that instrument maintenance logs are kept 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 or adjustment to instrument settings. 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., CCV 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 back up 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 laboratory 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.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Wet Chemistry	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Conductivity Meter (YSI)								
Cell							X	Replatinize cell when 1 µmho/cm range exceeds 90-100%, and when erratic readings cannot be corrected.
Check Standard Calibration	X							Make new solutions
UV/VIS Spectrophotometers (Shimadzu, Milton Roy)								
Wavelength					X			Verify wavelength(s)
Cells	X							Inspect daily for chips/scratches
Lamps							X	Replace if blown and realign
Ion Selective Electrodes (Orion)								
Electrode (Fluoride)							X	Polish.
Probe (Fluoride)							X	Fill with Single Junction Reference Electrode Filling Solution
Probe (pH)							X	Add 4*M* KCl solution if cell is low
Ionanalzyer (Orion)								
ATC						X		Verify against NIST thermometer
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 Class S weights
Balance						X		Checked and adjusted by service contractor
Weights						X		Checked against Class S weights
Centrifuges (Damon, Beckman Coulter)								
Centrifuge operation							X	Check warranty
Compartment							X	Clean
8" Drill Press benchtop (Chlorophyll grinder)								
Drill press operation							X	Check warranty
Thermometers								
Hach COD Reactor						X		Verify against NIST thermometer
Convection Ovens						X		Verify against NIST thermometer
Waterbaths								
Compartment							X	Clean with hot soapy water, fill with DI water
Thermometer						X		Verify against NIST thermometer

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Wet Chemistry continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Freezer								
Cleaning							X	Defrost and clean with hot soapy water
Thermometer						X		Verify against NIST thermometer
Cooler								
Cleaning							X	Sweep and mop
Stored samples		X						Discard samples by Discard List
Thermometer						X		Verify against NIST thermometer

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Nutrients	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
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.
IC Guard Column					X			Replace.
IC Eluent Pump			X					Check, replace if needed.
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; visually 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, Cold Fingers	X							Clean and check for cracks.
Timing							X	Check with watch, adjust as needed.
Racks			X					Clean.
pH Meter								
Probe			X					Inspect, add/replace KCl filling solution.
Probe	X							When not in use, keep lower end of probe in beaker of standard 6.86.
pH buffer standards							X	Prepare as needed.
ATC						X		Verify with NIST thermometer

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Nutrients continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Digital Balance								
Balance Pan	X							Clean.
Balance Level	X							Check that balance is level.
Calibration	X							Check with standard weights, each day used.
Balance						X		Contract service/cleaning
Weights						X		Verify against Class S weights
Ultrasonic Cleaner								
Solution in Tank	X							Maintain correct level; renew solution as needed.
Tank							X	Empty, clean with warm water, and wipe with non-abrasive cloth.
Reagent/Standard Refrigerator								
Temperature	X							Verify temp with thermometer.
Shelves					X			Clean.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Microbiology	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
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.
8-port valve thumbscrews	X							Hand-tighten.
IC sparger		X						Clean with mild soap and water.
Sparger & water traps	X							Empty.
Permeation dryer	X							Inspect for damage or water accumulation.
Combustion tube and/or catalyst							X	Change and/or repack.
Baseline							X	Adjust.
Microscope								
Lens							X	Clean.
Lamp							X	Replace.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Microbiology continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
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 Class S weights
Balance						X		Contract service/cleaning
Weights						X		Verify against Class S 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.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Metals	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
ICP – Optima 3000 XL								
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.
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.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Metals continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
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.
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.
Pipet tip	X							Check pipet tip for damage and repair or replace.
Argon gas (UHP or 99.996% purity)	X							Outlet gauge minimum pressure is 50 PSI and maximum 58 PSI.
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.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE										
Metals continued	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.		
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).		
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.		
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	Intensities (cps)
								Mg	4	>20,000
								Rh	102.9	>150,000
								In	114.9	>300,000
								Pb	208.0	>100,000
								Ba++/Ba+	69	<0.03
								CeO/Ce	155.9	<0.03
								Bkgd	220.0 amu	<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.		

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Volatile Organics	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Gad Chromatograph - VOA								
ELCD reactor temp.	X							Inspect daily.
ELCD reaction tube							X	Replace as needed.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Volatile Organics continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
ELCD propanol flow	X							Inspect daily and measure as needed.
ELCD propanol							X	Replenish as needed.
ELCD resin bed							X	Replace as needed.
Check PID sensitivity	X							Check daily standard and adjust as needed.
Change PID lamp							X	Replace.
Chromatographic column							X	Replace or cut as needed.
Leak check							X	Check column and fittings as needed/drift or poor sensitivity
Inlet Septum							X	Replace as needed.
Gas Cylinders	X							Inspect daily, change when pressure reads < 500 psi.
Hydrocarbon/Moisture Trap					X			Replace.
Teflon transfer line								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.
Purge and Trap								
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
LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Pesticides	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Gas Chromatograph - PESTICIDES								
Column							X	Replace.
Septum		X						Replace
Gas Cylinder	X							Inspect daily, change when pressure reads < 300 psi.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Pesticides continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Hydrocarbon/Moisture Trap						X		Replace.
Inlet liner			X					Replace
Automated Sample Processing System (GPC)								
Column							X	Resolvate.
Gas Cylinder	X							Inspect daily, change when pressure reads <300psi.
Methylene Chloride reservoir	X							Add solvent.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Semivolatile Organics	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
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	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								
Run Standard Spectrum tune							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

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Asheville Regional Laboratory	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
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.
Microscope								
Lens							X	Clean.
Lamp							X	Replace

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Asheville Regional Laboratory continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Orion 920A Meter								
pH Probe							X	Clean, add filling solution
Ammonia Probe		X						Change membrane & filling solution
ATC						X		Calibrate against NIST thermometer
Analytical Balance								
Balance Calibration	X							Verify calibration with Class S weights
Balance						X		Contract service/cleaning
Weights						X		Verify against Class S 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
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
Incubators (BOD)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Coils						X		Clean coils
Incubator (Coliform)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Coils						X		Clean coils
Refrigerators (sample storage)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Coils						X		Clean

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Washington Regional Laboratory	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
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; add DI water
Seals							X	Visually inspect and replace as needed
Timing				X				Check with stopwatch
BOD Meter								
Probe (electrolyte)		X						Change solution
Probe (membrane)							X	Replace membrane
Barometer			X					Calibrate
De-Ionizing Water System								
Canisters					X			Replace.
Conductivity	X							Check if within limits
Incubators (BOD)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Coils						X		Clean coils
Incubator (Coliform)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Coils						X		Clean coils
Ovens (residue)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Muffle Furnace (residue)								
Temperature	X							Check and document daily
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
pH Meter								
probe	X							Calibrate
							X	Clean
Refrigerators (sample storage)								
Temperature	X							Check and document daily

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Washington Regional Laboratory continued	SERVICE INTERVAL							
EQUIPMENT/INSTRUMENT	**D**	**W**	**M**	**Q**	**SA**	**A**	**AN**	**SERVICE**
Thermometer						X		Verify against NIST thermometer
Compartment			X					Clean
Coils						X		Clean
Turbidimeter								
Meter	X							Verify calibration with sealed standards
Lamp							X	Replace
Meter			X					Calibrate with sealed HF Scientific standards.
Vacuum Pump								
Oil						X		Change oil
Pump					X			Add oil and de-water
Water bath (Coliform)								
Thermometer						X		Verify against NIST thermometer
Bath				X				Clean and change water
Water							X	Add water
Water distillation system								
Still			X					Clean
Heating elements							X	Change
Microscope								
Lens							X	Clean.
Lamp							X	Replace.
Analytical Balance								
Balance Calibration	X							Verify calibration with Class S weights
Balance						X		Contract service/cleaning
Weights						X		Verify against Class S weights
Balance Pan	X							Clean
Balance Level	X							Check that balance is level

11.0 Quality Control Checks and Routines 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 QC Checks

QC 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 Laboratory Section 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, equipment blanks and trip blanks. Trip blanks are the only field QC required for sample submission to the Laboratory Section. When VOA samples are received without an associated trip 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 volatile organic samples. 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 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. Following is a brief description of these QC checks.

Batch
Environmental samples which are prepared and/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 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) and/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 sample 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.

Continuing Calibration Verification Standard (equivalent to Calibration Check Standard or CCC)
A Continuing Calibration Verification Standard (CCV) 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.
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, herbicides or acid extractable 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 to see if an obviously overlapping peak is causing an erroneously high result. If not 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 higher results. This approach is conservative relative to protection of the environment. The data user should be advised of the disparity between the results of the two columns.

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 or well water for 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 (or a dry tube purge as in the case of volatile organics analyses) 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 shall 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 sample 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 in 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 an 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 difference between the minimum and the maximum of a set of values.

11.2 Methods of Calculations for QC

11.2.1 Precision - Generating control limits for P and A

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 form 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, calculate range as follows:

$$\text{Range} = |C(_1) - C(_2)|$$

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:

$$\text{Control limit} = p + 3s$$
$$\text{Warning limit} = p + 2s$$

Control limits approximate a 99% confidence interval around the mean, while warning limits approximate a 95% confidence interval. Statistically, sixty-eight percent of all results should fall within one standard deviation of the mean. Statistically, seven consecutive results on one side or the other 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 laboratory. 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 and/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 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 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 error 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:

$$\text{Recovery (\%)} = \frac{\text{Conc. (or amt.) found}}{} \times 100$$

Conc. (or amt.) added

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 <u>more</u> 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[1,2] 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.

Table 11-1: Critical values for Grubb's T

Number of Data Points	Critical Value
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

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.

11.4 Method Detection Limits (MDL) and Practical Quantitation Limits (PQL)

The MDL defined below is adapted from 40 CFR Part 136, Appendix B, Revision 1.11 et seq. 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). MDL's 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 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 a significant change 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

a) 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).

b) 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).

1) 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.

2) If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

i) Obtain another sample with a lower level of analyte in the same matrix if possible.

ii) 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

a) 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.

b) 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.

1) 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.

2) 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.

Calculate the standard deviation (s) of the replicate measurements.

Compute the MDL, as follows:

$MDL = t_{(n-1,\ 1-\mu=0.99)}\ (s)$

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 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 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. An example format for documenting each MDL can be found in Figure 11-1.

11.6 Blind QC Check Sample Analysis

The laboratory is a participant in EPA's Performance Evaluation Study. Results of these tests will be summarized and included in the laboratory's QA report.

Figure 11-1: Example MDL Reporting Format

Method Detection Limit (MDL) Study

Laboratory Name:		**Analytical Method:**	
Analyst(s) Name(s):		**SOP#:**	
Date:		**Instrument:**	
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 Deviation s**	**MDL**	**PQL**

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 C.
PQL = 3 to 5 times the calculated MDL.

Comments: _____

Chemist's/Technician's Name	Signature	Date
Branch Manager's Name	Signature	Date
Lead Chemist's Name	Signature	Date
Quality Assurance Officer's Name	Signature	Date

12.0 Data Reduction, Verification and Reporting

In order to provide complete, accurate and verifiable results, all analytical data generated by the DWQ Laboratory Section 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 Laboratory Section'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;
- If the analytical instrument used generates hardcopy reports (e.g., strip charts, tabulated reports, etc.), the analyst will keep such raw data as part of the analysis records;
- Select the appropriate, method-specified formulae for calculating results. The formulae used are written in the standard operating procedures;
- 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 Laboratory Section 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.

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 properly 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.

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.

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, in appropriate 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 and/or method within the six analytical areas and two regional laboratories 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 Laboratory 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.

Soil/sediment concentration results for all laboratory sections 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.), 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 Laboratory Section'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 coeluded 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.

When data are reported from dual columns (as in gas chromatography), the default procedure is to report the highest 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 to note the discrepancy.

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:

$$\text{Concentration (ppb)} = \frac{(A_s)(V_t)(D)}{(\text{avgCF})(V_i)(S)}$$

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:

$$\text{Concentration (ppb)} = \frac{(A_s)(C_{is})(V_t)(D)}{(A_{is})(\text{avgRF})(S)}$$

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
avgRF 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:

$$\%\text{Recovery} = \frac{C_s - C_u}{C_n} \times 100$$

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:

$$RPD(\%) = 2\frac{|R_1 - R_2|}{R_1 + R_2} \times 100$$

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:

$$RSD(\%) = \frac{\text{Standard Deviation}}{\text{Mean Recovery}} \times 100$$

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 ug/L (for water samples) =

$$\frac{\text{Final extract or digestate conc. (ug/mL)} \times \text{Final extract or digestate volume (mL)}}{\text{Initial Sample Volume Extracted or Digested (L)}}$$

Concentration in ug/kg (for sediment samples) =

$$\frac{\text{Final extract or digestate conc. (ug/mL)} \times \text{Final extract or digestate volume (mL)}}{\text{Initial Sample Weight Extracted or Digested (kg)} \times \text{Dry Weight Correction Factor}}$$

C. The resulting sample and associated QC results are reviewed by the chemist, then if deemed acceptable, are uploaded to the DWQ STAR LIMS database or for organic analyses, typed onto a STAR report page. 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 appropriate qualification, comments or codes. 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 and/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. If the problem cannot be resolved immediately, the data may be rejected or reported with qualification.

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 errors shall be made by one line marked through the error. 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 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. Round off 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	
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 @ 25°C	
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 not 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 and/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 and/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 Laboratory DWQ STAR LIMS system. 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 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 DWQ STAR LIMS database by an individual familiar with it, but not involved in the original data reduction process (e.g., supervisor and/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 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 member of laboratory management or the QA/QC Coordinator using the procedures outlined in Section 13.

After verification of the data is complete, a macro is initiated by a Processing Assistant to check for completeness. When all results for a sample have been entered into the database, the results are printed from the DWQ STAR LIMS system into a final report. The hard copy report is then checked for data entry errors by a second Processing Assistant. The report is then sent to the branch managers or supervisors for release authorization.

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 12.3 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 DWQ STAR 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 Branch Managers for release authorization.

The branch managers or supervisors certify the hard copy reports by reviewing, dating and initialing. One report is retained with the original fieldsheets in the laboratory. The other report is mailed with copies of the fieldsheets to the client. All final sample results are archived in the DWQ STAR LIMS database 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. The results may be qualified as follows:

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).

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 coliform colonies exceeds the ideal ranges indicated by the method. These ideal ranges are defined in the method as:

Fecal coliform 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 a total of the counts from all countable filters reported per 100 ml.

5. Too many colonies were present; too numerous to count (TNTC), the numeric value represents the maximum number of counts typically accepted on a filter membrane (60 for fecal 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.

Note: A "B" value shall be accompanied by justification for its use denoted by the numbers listed above (ex. B1, B2, etc.)

C Total residual chlorine was present in sample upon receipt in the laboratory; value not accurate (cyanide, phenol, NH_3, TKN, coliform, 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.

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 (ex. 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; or

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, 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.

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 analysis 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.*

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.

1. Holding time exceeded prior to receipt by lab.
2. Holding time exceeded following receipt by lab.

S Not enough sample provided to prepare and/or analyze a method-required matrix spike (MS) and/or 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

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 method blank. Note: The value in the blank shall not be subtracted from the associated samples.

Z The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

P Elevated PQL* due to matrix interference and/or sample dilution.

Y Elevated PQL* due to insufficient sample size.

The decision to qualify a result on these factors is at the discretion of the authorizing supervisor and must comply with Laboratory Section 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 (i.e., lab number) 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 Branch Manager or their designee. Persons designated to sign reports include the Section Chief, Branch Managers, Unit Supervisors, and the QA/QC Officer.

An example report can be found in Figure 12.2. 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.

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 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 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), 215 North Blount 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, 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 requester's 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 where appropriate. These file identification numbers reflect either the date the sequence was initiated, the order in which the samples were analyzed and/or the sample identification and log numbers given by the client and listed on the DWQ STAR LIMS.

The 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.

The DWQ STAR LIMS data resides on the main Laboratory Section server. The server is programmed to backup daily. These daily tapes are overwritten every two weeks. A full back up of this server occurs monthly. The monthly tapes are managed by the LAN specialist and are stored in the room in which the server is located in a fireproof cabinet.

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.

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. Notebooks are not destroyed. A master log is kept of all notebooks (e.g., standard logbooks and instrument logbooks) that are issued. At a minimum, this log includes:

- Notebook Number - Each notebook is issued a unique number that is determined sequentially.
- Used for - Purpose and department of notebook.
- Replaces notebook number - Place the number of the notebook that the issued notebook will replace if applicable.
- Date of issue - This is the date that the notebook is released.
- Issued to - The analytical unit the notebook is released to.

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 error. 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.

Figure 12.1 Organics

In the organic areas, the following information is verified when applicable to the method being reviewed.

- Check dates (e.g., extraction, calibration, analysis) and verify that holding times are met.
- All criteria for calibration, instrument tuning, internal standard areas, retention times, surrogate recoveries and analytical quality control results are checked.
- Check all 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.
- All calculations such as total volatile hydrocarbons, soil concentrations, percent recoveries and dilutions are checked.
- All irregularities are properly documented and if necessary data flagged when pre-established control limits are not met.

Figure 12.2 Inorganics and Microbiology

In the inorganic and microbiological analytical areas, the second analysts check the following items prior to results being entered into the data management system.

- Check dates (extraction, digestion, calibration, incubation, analysis) and verify that holding times are met.
- All calibration criteria are met.
- Check all 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.
- Check all calculation or data entry into calculation programs designed to calculate final results. Calculated results are checked against data bench worksheets for transcription errors.
- Check to be sure any irregularity is documented and; if necessary, data flagged when pre-established control limits are not met.
- Check reasonableness of data relationships (e.g., ammonia nitrogen results should not exceed total Kjeldahl nitrogen results).

Figure 12.2 Example report.

DIVISION OF WATER QUALITY

Chemistry Laboratory Report / Water Quality

COUNTY : MECKLENBURG
RIVER BASIN: CTB34

REPORT TO : MRO Regional Office

Other : -
COLLECTOR(S) : BLOVE

PRIORITY
[X] AMBIENT
[ ] COMPLIANCE
[ ] EMERGENCY
[ ] QA
[ ] CHAIN OF CUSTODY

VISIT ID
V12155

[W] SAMPLE TYPE
[X] STREAM
[ ] LAKE
[ ] ESTUARY
[ ] EFFLUENT
[ ] INFLUENT

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

Data Released :
Date Reported:

Estimated BOD Range:

Station Location: SUGAR CRK AT NC 51 AT FINEVILLE

Seed: _____ Chlorinated: _____

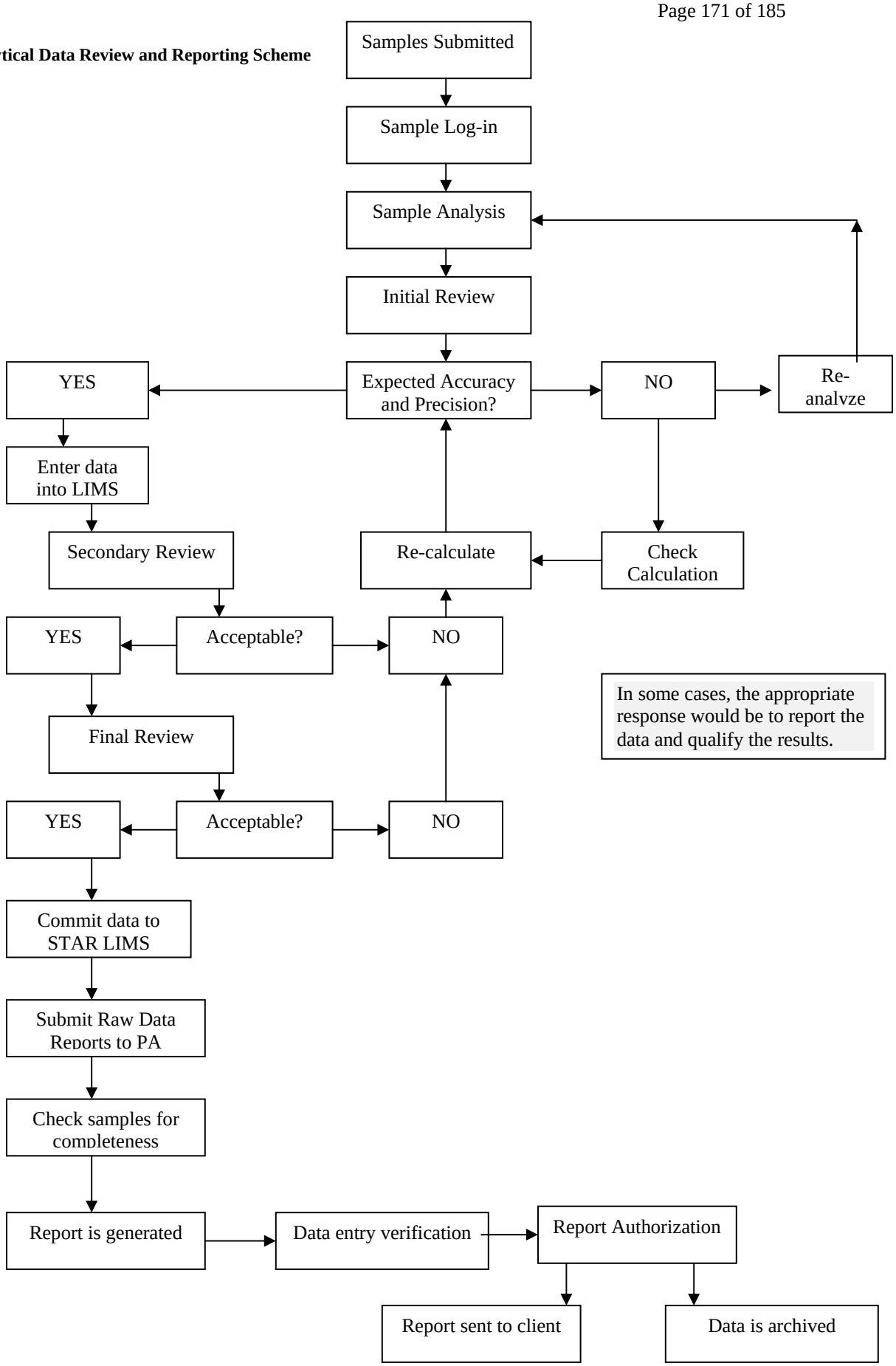
Remarks:

Station#	Date Begin (yy/mm/dd)	Date End (yy/mm/dd)	Time Begin	Time End	Depth - DM, DB, DBM	Value Type - A, H, L	Composite - T, S, B
C9050000	20030102		1030		0.1		

	BOD 310		mg/L		Chloride 940		mg/L	X	N-B as N 610	0.02	mg/L		Li-Lithium 1132
	COD High 340		mg/L		Chl a: Tri 32217		ug/L	X	TKN an N 625	0.50	mg/L		Mg-Magnesium 927
	COD Low 335		mg/L		Chl a: Corr 32209		ug/L	X	NO2 plus NO3 as N 630	2.9	mg/L		Mn-Manganese 1055
X	Coliform: MF Fecal 31616	150 Q1	/100ml		Pheophytin a 32213		ug/L	X	P. Total as P 665	0.28	mg/L		Na-Sodium 929
	Coliform: MF Total 31504		/100ml		Color: True 80		cu		PO4 as P 70507		mg/L		Arsenic: Total 1002
	Coliform: tube Fecal 31615		/100ml		Color: (pH) 83 pH=		cu		P. Dissolved as P 666		mg/L		Se-Selenium 1147
	Coliform: Fecal Strep 31673		/100ml		Color: pH 7.6 82		cu		K-Potassium		mg/L		Hg-Mercury 71900
	Residue: Total 500		mg/L		Cyanide 720		mg/L		Cd-Cadmium 1027		ug/L		Ba_Barium
	Volatile 505		mg/L		Fluoride 951		mg/L		Cr-Chromium Total 1034		ug/L		Organochlorine Pesticides
	Fixed 510		mg/L		Formaldehyde 71880		mg/L		Cu-Copper 1042		ug/L		Organophosphorus Pesticides
	Residue: Suspended 530		mg/L		Grease and Oils 556		mg/L		Ni-Nickel 1067		ug/L		
	Volatile 535		mg/L		Hardness Total 900		mg/L		Pb-Lead 1051		ug/L		Acid Herbicides
	Fixed 540		mg/L		Specific Cond 95		umhos/cm2		Zn-Zinc 1092		ug/L		
	pH 403		units		MBAS 38260		mg/L		V-Vanadium		ug/L		Base/Neutral & Acid Extractable Org
	Acidity to pH 4.5 436		mg/L		Phenols 32730		ug/L		Ag-Silver 1077		ug/L		TPH Diesel Range
	Acidity to pH 8.3 435		mg/L		Sulfate 945		mg/L		Al-Aluminum 1105		ug/L		
	Alkalinity to pH 8.3 415		mg/L		Sulfide 745		mg/L		Be-Beryllium 1012		ug/L		Purgeable Organics (VOA bottle req
	Alkalinity to pH 4.5 410		mg/L		Boron				Ca-Calcium 916		mg/L		TPH Gasoline Range
	TOC 680		mg/L		Tannin & Lignin		ug/L		Co-Cobalt 1037		ug/L		TPH BTEX Gasoline Range
X	Turbidity 76	16	NTU		Hexavalent Chromium		ug/L		Fe-Iron 1045		ug/L		Phytoplankton
	Coliform Total Tube		"/100 mls		Bicarbonate		mg/L						
					Carbonate		mg/L						

COMMENTS:

Figure 12.3 - Analytical Data Review and Reporting Scheme



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 DWQ Laboratory Section 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 Laboratory Section, 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 for details of failures. All other significant observations that do not conform with accepted practices or policies are documented and reported along with analytical results.

13.1.1 Sample Anomaly Report (SAR) Form

Corrective actions necessary to obtain acceptable results are implemented and documented. Corrective action at the bench level is documented on the raw data or through the use of a SAR form (Figure 13.1). The action is approved by the Supervisor, Branch Manager, and QA Officer and a copy is placed in each applicable analytical batch folder.

A Sample Anomaly Report documents laboratory quality control and quality assurance issues that warrant further investigation. These forms are logged into a SCUR/SAR database with the original retained in the sample report files and copies provided to the client and any applicable analytical data folders.

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 logged into a SCUR/SAR database with the original retained in the sample report files and copies provided to the client and any applicable analytical data folders. 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 and/or the analyst will 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 the following 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 and/or re-analyze 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.

13.4 Systematic Problems

Those problems of a procedural/system nature generally require the supervisor's and/or branch 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. If previous data is affected, 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. 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 branch 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 so notes it on the raw data and/or on a SAR form. This information can then be supplied to the client in the form of a footnote or on a Sample Anomaly Report.

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 to improve service to and relationships with clients. The Laboratory Section's goal is expeditious resolution of complaints.

The Laboratory Section is committed to resolving complaints and implementing suggestions for improvement. All informal complaints, suggestions or requests for information are directed to the appropriate staff for resolution. If immediate resolution cannot be attained, the matter is passed through the chain-of-command, ultimately to the Section Chief who may investigate and direct the resolution. 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 Laboratory 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.

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 form 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 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. 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, 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.

Figure 13.1 Sample Anomaly Report (SAR) Form

NC DENR/DWQ Chemistry Laboratory
Sample Anomaly Report (SAR)

Report to: _____

Lab Number: _____ Sample ID: _____

Station Location: _____ County: _____ Region: _____

Sample Type: _____ Priority: _____ Collector: _____

Date collected: _____/_____/_____ Date received: _____/_____/_____ Date analyzed: _____/_____/_____

Affected Parameter(s): _____

Analytical Area (check one):

- ❑ WCH
- ❑ NUT
- ❑ METALS
- ❑ MICRO
- ❑ VOA
- ❑ PEST
- ❑ SVOA

The following anomalies occurred (**check all that apply**):

- ❑ **Samples**
- ❑ Improper container used
  - ❑ VOA vials with headspace
  - ❑ Sulfide samples with headspace
- ❑ Samples not received, but listed on fieldsheet
- ❑ Samples received, but not listed on fieldsheet
- ❑ Mislabeled as to tests, preservatives, etc.
- ❑ Holding time expired
  - ❑ Prior to receipt in lab
  - ❑ After receipt in lab
- ❑ Insufficient quantity for analysis
- ❑ Sample exhibits gross non-homogeneity
- ❑ Sample not chemically preserved properly
  - ❑ pH out of range (record pH): _____
  - ❑ Improper chemical
- ❑ Residual chlorine present in sample
- ❑ Color interference
- ❑ Heavy emulsion formed during extraction
- ❑ Sample bottle broken in lab - no reportable results

- ❑ **Quality Control**
- ❑ Instrument failure – no reportable results
- ❑ Analyst error – no reportable results
- ❑ Surrogates
- ❑ None added
- ❑ Recovery outside acceptance limits
- ❑ Spike recovery
- ❑ None added
- ❑ Recovery outside acceptance limits
- ❑ Failed to meet criteria for precision
- ❑ Internal standards
- ❑ Blank contamination
- ❑ QC data reported outside of controls (i.e. QCS, LCS)
- ❑ Incorrect procedure used
- ❑ SOP intentionally modified with QA and Branch Head approval
- ❑ Invalid instrument calibration
- ❑ Elevated detection limits due to:
- ❑ Insufficient sample volume

- ❑ **Other** (specify):_____

Comments: _____

Corrective Action:

- ❑ Samples were rejected by DWQ Lab. Authorized by: _____ Date: _____/_____/_____
- ❑ Accepted and analyzed after notifying the collector or contact person and determining that another sample could not be secured.
- ❑ Sample(s) on hold until: _____
- ❑ Sample reported with qualification. Data qualification code used: _____
- ❑ Other (explain): _____

Notification Required (circle one)? Yes No
Person Contacted: _____ Date: _____/_____/_____

Form completed by: _____ Date: _____/_____/_____

Lead Chemist Review (initial):

- ❑ BIOCHEM _____
- ❑ METALS _____
- ❑ PEST _____
- ❑ VOA _____
- ❑ SVOA _____

Branch Head Review (initial): _____
QA/QC Review (initial): _____

Logged into database by (initial): _____

Figure 13.2 Sample Condition Upon Receipt (SCUR) Report

NC DENR/DWQ Chemistry Laboratory
Sample Condition Upon Receipt Anomaly Report (SCUR)

Report to: _____

Lab Number: _____

Sample ID: _____ Station Location: _____

County: _____ Region: _____

Collector: _____ Date collected: _____/_____/_____ Date received: _____/_____/_____

Priority: _____ Sample Type: _____

Affected Parameter(s): _____

The condition of these samples were not acceptable because (**check all that apply**):

- ❑ **Coolers**
- ❑ Samples were not received on wet ice
- ❑ No temperature blank submitted (see comments):
  - ❑ Sample T° reading : _____°C
  - ❑ Cooler T° reading: _____°C
- ❑ Temperature >6°C. T° reading: _____°C
- ❑ Samples frozen

- ❑ **Containers**
  - ❑ Leaking
  - ❑ Broken
  - ❑ Without labels
  - ❑ VOA vials with headspace
  - ❑ Sulfide samples with headspace

- ❑ **Container Labels**
  - ❑ Not the same ID/info. as on COC
  - ❑ Not the same ID/info. as on fieldsheet
  - ❑ Incomplete. Missing the following:
    - ❑ Station #/Sample ID
    - ❑ Collection date
    - ❑ Collector
    - ❑ Analysis
    - ❑ Preservative
    - ❑ Other: _____
  - ❑ Markings smeared or illegible
  - ❑ Torn

- ❑ **Samples (affected samples are described below)**
  - ❑ Samples not received, but listed on fieldsheet
  - ❑ Samples received, but not listed on fieldsheet
  - ❑ Samples not received, but listed on COC
  - ❑ Samples received, but not listed on COC
  - ❑ Mislabeled as to tests, preservatives, etc.
  - ❑ Holding time expired
  - ❑ Improper container used
  - ❑ Insufficient quantity for analysis

- ❑ **Chain of Custody**
  - ❑ No custody seals
  - ❑ Custody seals not intact
  - ❑ Not relinquished.
    - ❑ No date/time relinquished
    - ❑ No signature
  - ❑ Incomplete information

- ❑ **Documentation**
- ❑ Fieldsheet wet/illegible
- ❑ Fieldsheet incomplete: _____
- ❑ Records not written in indelible ink
- ❑ Sample(s) submitted without fieldsheet

- ❑ **Other (specify)**: _____
  _____
  _____

Comments: _____
_____

Corrective Action:

- ❑ Samples were rejected by DWQ Lab. Authorized by: _____
- ❑ Accepted and analyzed per collector's request after notifying the collector.
- ❑ Accepted and analyzed after notifying the client and determining that another sample could not be secured.
- ❑ Sample(s) on hold until: _____
- ❑ Sample(s) accepted and analyzed. No notification required.
- ❑ Other (explain): _____

Person Contacted: _____ Date: _____/_____/_____

Form completed by: _____Date: _____/_____/_____

Lead Chemist Review (initial):

- ❑ BIOCHEM _____
- ❑ MET _____
- ❑ VOA _____
- ❑ SVOA _____
- ❑ PEST_____

Branch Head Review (initial): _____
QA/QC Review (initial): _____

Logged into database by (initial): _____

14.0 Performance and Systems Audits

Internal and external audits are conducted regularly within the DWQ Laboratory Section to ensure that the guidance provided in this document and in other related documents is followed. Internal audits are performed by the QA department, which is responsible for all QA/QC functions in the laboratory, and/or 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 DWQ Laboratory Section (generally EPA Region 4) to provide an independent and unbiased review of laboratory operations.

There are two types of audits: systems audits and performance audits.

1) Systems 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 require the analysis of blind samples or other samples whose values are not known to the analytical areas. These results are used to evaluate the accuracy of the laboratory analytical system.

14.1 Systems 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 and/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 requirements, problem troubleshooting or issues that arise from other audits.

The QA/QC Coordinator conducts several systems audit during each calendar year. During these audits, one or more components of the laboratory will be reviewed to determine if that part is functioning in compliance with the Laboratory Section Quality Management Plan, the Laboratory Section 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 will conduct the audits.

(3) The audit will consist of the submittal of blind samples and/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:

(i) 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 (PT) samples or blind samples.

(vi) 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 sample for analysis and/or conduct on-site inspections. It is the Laboratory Section'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 include:

(1) EPA, Region IV; for selected systems, on an 18-36 month basis, depending on budget constraints

(2) USGS; selected systems; per-project basis

14.2 Performance Audits

The laboratory is involved in external performance audits conducted annually through the analysis of PT samples provided by this lab and a third party.

14.2.1 Blind Sample Audits

The QA/QC Coordinator conducts internal performance evaluations using commercially prepared samples as blind samples. The results of these audits will be documented and reported to the supervisors, branch managers and Section Chief so that any necessary adjustments can be made.

Blind sample audits may be initiated upon observed or suspected problem with specific system and split sample analyses by specific, per-project agreement with regulatory and commercial laboratories. Reports of results, deficiencies and corrective actions are communicated as with internal system audits, with the addition of reports to affected external organizations.

Blind sample audits are performed by submitting QC samples to the analyst. The true values are only made known after the test is complete. Blind sample audits are carried out by the QA/QC Coordinator, clients and certifying agencies as necessary to assure the laboratory is capable of achieving success with a blind QC sample.

14.2.2 Performance Testing samples

The lab participates in an annual Section-wide internal Performance Testing (PT) program to evaluate methods that are not commonly included in the PT studies.

Holding time begins when the vial is opened. Full volume PTs 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.

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), 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.

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 DWQ 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.

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. Managers 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 quarterly basis are not components of larger systematic concerns. The quarterly 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 Monthly 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 monthly 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 may be required. The response must address the reason for any "unacceptable" or "check for error" result. In some cases it 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 reviewer is not expected to pursue the correctness of every reference in the file contents, but concentrates on the internal consistency of the data package. Areas for review 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 file 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 quarterly QA report is prepared by the QA/QC Coordinator. This information is circulated to the Section Chief, Branch Managers and unit supervisors. 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 Monthly QA Report to Management Format

QA MONTHLY REPORT TO MANAGEMENT

LABORATORY:
ANALYTICAL UNIT:
PERIOD COVERED:
PREPARED BY:

TO: Steve Tedder, Section Chief
CC: Branch Manager(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)
- Total number of SARs:
- Total number of SCURs:
- Number of unresolved SARs:
- Highlights:

C. MDLs/IDOCs
- MDLs completed:
- MDLs due:
- 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

H. NEXT MONTH (Items planned for next month)

16.0 Selected References

1. "Definition and Procedure for the Determination of the Method Detection Limit- Revision 1.11", 40 CFR Part 136, Appendix B.

2. Handbook for Analytical Quality Control in Water and Wastewater, EPA 600/4-79-019, March 1979.

3. 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.

4. 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.

5. Method for the Determination of Organic Compounds in Drinking Water, Supplement I, EPA 600/4-90/020, July 1990.

6. Standard Methods for the Examination of Water and Wastewater (designated SM), 18th Edition, American Public Health Association, Washington, DC, 1992.

7. Standard Methods for the Examination of Water and Wastewater (designated SM), 19th Edition, American Public Health Association, Washington, DC, 1995.

8. Standard Methods for the Examination of Water and Wastewater (designated SM), 20th Edition, American Public Health Association, Washington, DC, 1998.

9. Code of Federal Regulations, Title 40, Part 136, U.S. Government printing office, Washington, D.C., July 1993.

10. Chemical Hygiene Plan, North Carolina Division of Water Quality, Laboratory Section - Central Laboratory, October 1, 1997.

11. Chemical Hygiene Plan, North Carolina Division of Water Quality, Laboratory Section - Washington Regional Office, April 2003.

12. Chemical Hygiene Plan, North Carolina Division of Water Quality, Laboratory Section - Asheville Regional Office, March 5, 2001.

APPENDIX 4:

STREAM FISH COMMUNITY ASSESSMENT PROGRAM (SFCAP) STANDARD OPERATING PROCEDURES (SOP)

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STANDARD OPERATING PROCEDURE
BIOLOGICAL MONITORING

STREAM FISH COMMUNITY ASSESSMENT PROGRAM

NORTH CAROLINA
DEPARTMENT OF ENVIRONMENT
AND NATURAL RESOURCES
Division of Water Resources
Environmental Sciences Section
Biological Assessment Branch

December 01, 2013

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REVISION LOG

STREAM FISH COMMUNITY ASSESSMENT PROGRAM
STANDARD OPERATING PROCEDURE
*Actions older than five years may be removed from this log.

Date Edited	Editor	Version Edited	Section Edited	Changes/updates
11/19/2013	Bryn H. Tracy	Ver.5	Cover page and footers	Updated document date to December 15, 2013 and version number to Version 5.
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	All references to Division of Water Quality (DWQ) were changed to Division of Water Resources (DWR).
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	All references to Biological Assessment Unit (BAU) and Intensive Survey Unit were changed to Biological Assessment Branch (BAB) and Intensive Survey Branch.
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	Corrected spelling and typographic mistakes
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	Updated photographs
11/19/2013	Bryn H. Tracy	Ver. 5	Page 2, Revision Log	Added a Revision Log
11/19/2013	Bryn H. Tracy	Ver. 5	URL links	All Internet hyperlinks were checked and functioned correctly.
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	Changed Environmental Biologist III to Sr. Environmental Specialist
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	Changed responsibility of the program from Environmental Biologist III and Environmental Biologist II to Sr. Environmental Specialist to reflect existing work responsibilities and staffing resources.
11/19/2013	Bryn H. Tracy	Ver. 5	Page 4, Signature and Approval	Updated
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	Changed Microsoft Access® 2000 to 2010.
11/19/2013	Bryn H. Tracy	Ver. 5	Objectives	Changed ". . . *more than 1,000 samples from 700 sites . .* " to "*more than 1,700 samples from more than 900 sites . .* ".
11/19/2013	Bryn H. Tracy	Ver. 5	Figure 2	Updated map to reflect number of sites that have been sampled through 12/31/2013.
11/19/2013	Bryn H. Tracy	Ver. 5	Species Richness and Composition, Metric No. 4, Number of Species of Sunfish, Bass, and Trout (Inner Piedmont, Foothills, and Eastern Mountains)	Added *Pomoxis* to correct a mistake in Version 4
11/19/2013	Bryn H. Tracy	Ver. 5	Table 4	Added Southern Brook Silverside, Golden Topminnow, Bluefin Killifish, Least Killifish, Carolina Fantail Darter, Roanoke Logperch
11/19/2013	Bryn H. Tracy	Ver. 5	Table 4	Removed Dusky Darter (incorrect state listing)
11/19/2013	Bryn H. Tracy	Ver. 5	Table 5	Added Roanoke Logperch
11/19/2013	Bryn H. Tracy	Ver. 5	Entire document	NCDENR (2003) updated to NCDENR (2011)
11/19/2013	Bryn H. Tracy	Ver. 5	Figure 4	Previous figure deleted and a new figure was inserted to reflect current basin monitoring cycles
11/19/2013	Bryn H. Tracy	Ver. 5	Field Water Quality Measurements	Deleted: "*The only acceptable exception is pH. Most field pH meters are not waterproof; therefore, pH is measured from a water sample within five minutes of sample collection*" because it is no longer a valid statement.
11/19/2013	Bryn H. Tracy	Ver. 5	Table 10	Re-ordered parameters.
11/19/2013	Bryn H. Tracy	Ver. 5	Field Water Quality Measurements	Deleted reference to a two point calibration for specific conductance. Specific conductance calibration standards changed from 147 and 718 µS/cm to 500 and 1,000 µS/cm.
11/19/2013	Bryn H. Tracy	Ver. 5	Field Water Quality Measurements	Updated calibration paragraph
11/19/2013	Bryn H. Tracy	Ver. 5	Field Water Quality Measurements	Changed : "*Meters should be checked, . . .*" to "*Meters may be checked, . . .*"
11/19/2013	Bryn H. Tracy	Ver. 5	Acquired Data	Added -- http://water.usgs.gov/osw/streamstats/north_carolina.html
11/19/2013	Bryn H. Tracy	Ver. 5	Components of the QA/QC Plan	Re-wrote how samples are randomly chosen for QA.
11/19/2013	Bryn H. Tracy	Ver. 5	LeGrand et al. 2004	Changed to Legrand et al. 2012
11/19/2013	Bryn H. Tracy	Ver. 5	Table 11	Updated to reflect current listings in LeGrand et al (2012).
11/19/2013	Bryn H. Tracy	Ver. 5	Appendix 2	Deleted "Subbasin" and Added "8 Digit HUC".

Date Edited	Editor	Version Edited	Section Edited	Changes/updates
11/19/2013	Bryn H. Tracy	Ver. 5	Appendix 3	Updated to reflect existing field data sheet that is used and an example of its use.
11/19/2013	Bryn H. Tracy	Ver. 5	Appendix 4	Updated with Version 06/05/2012.
11/19/2013	Bryn H. Tracy	Ver. 5	Appendix 5	Updated with Revision 8 to reflect existing habitat assessment field data sheet – Mountain/Piedmont streams that is used.
11/19/2013	Bryn H. Tracy	Ver. 5	Appendix 6	Updated with Revision 9 to reflect existing habitat assessment field data sheet – Coastal Plain streams that is used.
11/19/2013	Bryn H. Tracy	Ver. 5	Appendix 8	Updated to reflect existing fish community report that is generated from the Microsoft Access® 2010 database.

Standard Operating Procedures
Stream Fish Community Assessment Program

Environmental Sciences Section
Biological Assessment Branch

NORTH CAROLINA DEPARTMENT OF ENVIRONMENT
AND NATURAL RESOURCES
Division of Water Resources

This report has been approved for release

Dianne Reid
Environmental Sciences Section Chief
Date: December 01, 2013

INTRODUCTION

It is the purpose of this manual to provide details on standard operating procedures of the Biological Assessment Branch (BAB) of the Division of Water Resources (DWR or Division) for the collection and analysis of stream fish community assessment data. Consistency in data collection and analysis is the cornerstone for evaluating biological integrity. The procedures provided are a synthesis of widely used methods and methods developed from the experience of personnel within the Branch. These methods have been shown to provide repeatable and useful data for water quality evaluation.

This document will be reviewed regularly and revised as necessary. The prior approved version (Version 4) was dated August 01, 2006. All current employees and new employees within the Branch will be provided with this document to serve as a guideline of the Branch's activities, methods, and procedures. Revisions to this document will be provided to each employee and it will be the responsibility of the Sr. Environmental Specialist to insure that the procedures are current.

The standard operating procedures (SOP) and quality control procedures (QC) in this manual will be the basis for all stream fish community assessment monitoring and the subsequent data provided in memoranda and reports prepared by the Biological Assessment Branch. Deviations from these procedures for unusual sampling situations shall be documented in the appropriate report or memorandum.

SAFETY PROGRAM

The Biological Assessment Branch is required to sample throughout North Carolina at times and places where medical facilities may not be readily available. It is imperative that all employees are instructed in and follow safety precautions when using sampling equipment and hazardous materials. The Environmental Sciences Section has a Safety Committee which is responsible for maintenance and development of current safety procedures. The Committee also maintains the safety standard operating procedures document which all personnel should be familiar. All personnel involved in electrofishing activities should be trained in First Aid and CPR and should be familiar with standard electrofishing safety procedures.

Sampling conditions are the primary safety factor to be considered for field work. If any field conditions such as high flows or thunderstorms raise the question of whether a sample can be safely collected, then decisions should always be made with the safety of personnel of prime concern. This same concern for safety of staff must be of primary importance when scheduling the amount of time to be spent in the field. Long days combined with strenuous effort increase the probability of accidents occurring. "**Safety first**" must always be the rule.

Employees should promptly report on-the-job accidents to the Branch Supervisor. If an accident occurs during field operations, the first responsibility of the team leader is to get first aid treatment for the injured employee; their second responsibility is to promptly notify the Branch Supervisor. The Safety Committee maintains a written record of accidents.

STUDY PLANS

All investigations conducted by the Biological Assessment Branch will follow a written study plan including but not limited to the:

- **Introduction** - Identify the nature and history of the area being investigated and the person or agency requesting the study.
- **Objectives** - The purpose of the investigation.
- **Sampling Location Selection** – Location of the sampling points is of extreme importance in the initiation of stream fish community assessment monitoring. The variables in watersheds are many and should be considered in as much detail as possible before sites are selected to monitor any body of water. Land use (i.e., urban, rural, forested, agricultural, and industrial) should be considered when locating sample sites, because man-made activities significantly affect the amount of sedimentation, nutrients, and organic or inorganic compounds entering a given segment of a river or stream. The location of permitted dischargers should be reviewed, using

the database provided by the Division's Basinwide Information Management System. Discussion of the proposed study with regional office personnel can also provide additional information useful for determining sampling locations. Pre-study planning of this nature will enhance data analyses and interpretation after the collections have been made.

- **Methods** - Sampling techniques should be listed with reference to those described in this manual. Any deviation from these standard methods must be noted and described.
- **Analytical Requirements** - All physico-chemical variables to be collected and analyses that will be required should be noted.
- **Logistics** - Shall include estimates of manpower requirements, equipment needed, time requirements, methods of sample transport to laboratories, *etc*. The study plan must be submitted and approved by the Branch Supervisor prior to conducting the investigation.

A study is complete when a report or memorandum is sent to and approved by the appropriate level of management within the Division (typically the Environmental Sciences Section Chief). Each memorandum should contain these sections: an Introduction or Background, Sampling Sites, Methods, Results and Discussion, and Summary or Recommendations. Any figures, maps, and photographs needed to allow a reader to easily locate the sampling sites should also be included. When the report or memorandum is approved, a Biological Assessment Branch file number is assigned. Finally, the report or memorandum is filed in a Projects File that is organized by basin and subbasin.

STREAM FISH COMMUNITY ASSESSMENT PROGRAM

OBJECTIVES

North Carolina consists of 17 major river basins (Figure 1). Each of these basins is assessed every five years to support the Planning Section's Basinwide Water Quality Management Plans. The Division utilizes several water quality programs and tools to assess the quality of the state's waters. One of the more recently developed (and still developing) programs is the Stream Fish Community Assessment Program. The primary objective of this program is to provide fish community ratings for wadeable streams to the Basinwide Planning Section for use support determinations and for the Section's Basinwide Water Quality Management Plans.

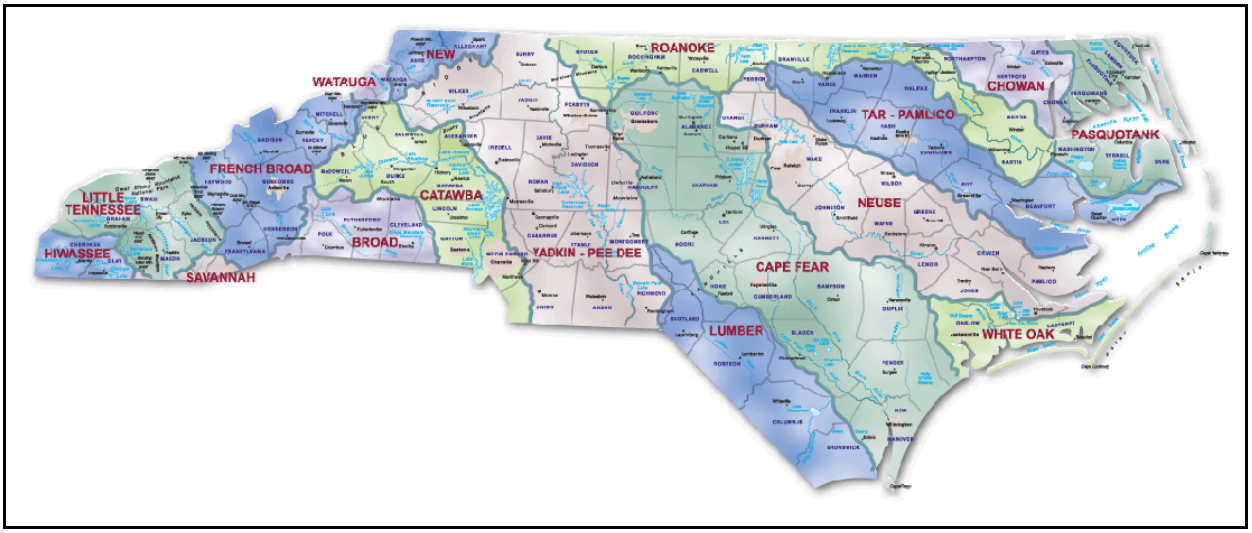

Figure 1. Major river basins of North Carolina.

Secondary objectives of the Program are to provide data suitable for supporting these DWR activities:

- Planning Section
  - ❖ Biennial 303(d) and 305(b) reporting to EPA, including identification of areas of impairment or degradation,
  - ❖ TMDL development,
  - ❖ Prioritization of restoration activities, and
  - ❖ Background information for Use Attainability studies such as trout survival and propagation waters, High Quality Waters, and Outstanding Resource Waters.
- Surface Water Protection Section
  - ❖ Identification of background levels of constituents for determination of NPDES permit limits, and
  - ❖ Identification of dischargers causing unacceptable impacts.
- Regional Offices
  - ❖ Background information to assist with water quality management activities in each region.

The Stream Fish Community Assessment Program was designed as an additional basinwide assessment tool and has been in existence since 1991. It's core mission is to sample a set of fixed sites on lower Strahler order wadeable creeks, streams, and rivers on a five-year rotating basis to support the DWR's Basinwide Management Plan Program. To date, more than 1,700 samples from more than 900 sites have been assessed (Figure 2), primarily in the Piedmont and Mountains. Most of the stations are located at bridge crossings or other public accesses and are accessible by land. Nonwadeable and higher Strahler order rivers, estuaries, and reservoirs are not monitored. The program compliments other DWR programs such as the Benthic Macroinvertebrate and Ambient Monitoring System programs which tend to focus monitoring efforts on larger waterbodies and watersheds.

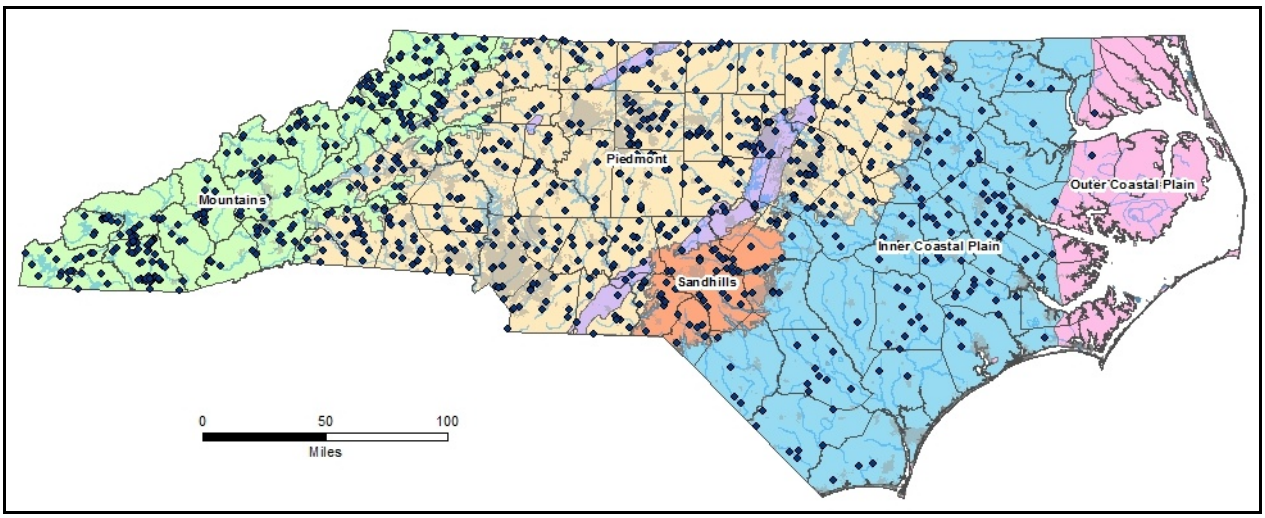

Figure 2. Stream fish community sampling sites, 1991 – 2012. Colored regions indicate select Level III and IV ecoregions and dots indicate fish community sampling sites.

THE NORTH CAROLINA INDEX OF BIOTIC INTERGRITY

The Division has been monitoring the biological integrity of stream fish communities since the early 1990s. The biological monitoring tool that is used is referred to as the North Carolina Index of Biological Integrity (NCIBI). The NCIBI method was developed for assessing a stream's biological integrity by examining the structure and health of its fish community. The North Carolina Administrative Code defines *Biological Integrity* as: " . . . *the ability of an aquatic ecosystem to support and maintain a balanced and indigenous community of organisms having species composition, diversity, population densities, and functional organization similar to that of reference conditions*" (15A NCAC 02B .0200; NCAC 2004). The NCIBI is a modification of the Index of Biotic Integrity (IBI) initially proposed by Karr (1981) and Karr, *et al*. (1986).

The NCIBI incorporates information about species richness and composition, trophic composition, fish abundance, and fish condition. The NCIBI summarizes the effects of all classes of factors influencing aquatic faunal communities such as water quality, energy source, habitat quality, flow regime, and biotic interactions. While any change in a fish community can be caused by many factors, certain aspects of the community are generally more responsive to specific influences. Species composition measurements reflect habitat quality effects. Information on trophic composition reflects the effect of biotic interactions and energy supply. Fish abundance and condition information indicates additional water quality effects. It should be noted, however, that these responses may overlap. For example, a change in fish abundance may be due to decreased energy supply or a decline in habitat quality, not necessarily a change in water quality.

The scores derived from this index are a measure of the ecological health of the waterbody and may not directly correlate to water quality. For example, a stream with excellent water quality, but with poor or fair fish habitat, may not be rated excellent with this index. However, a stream which rated excellent on the NCIBI should be expected to have excellent water quality.

APPLICATION OF THE NCIBI

The NCIBI is continually being refined for greater applicability to wadeable streams in North Carolina. Currently, the NCIBI is applicable **only** to **streams** that are **wadeable** from one shoreline across to the other and for a distance of 600 feet. The NICIBI is only applicable to wadeable streams in the Western and Northern Mountains (French Broad, Hiwassee, Little Tennessee, New, and Watauga River basins), the Inner Piedmont, Foothills, and Eastern Mountains (Broad, Catawba, Savannah, and Yadkin (exclusive of the Sand Hills) River basins); and the Outer Piedmont (Cape Fear, Neuse, Roanoke, and Tar River basins).

The delineations of the Mountains, Piedmont, and Sand Hills in these river basins are based upon a North Carolina State University Co-operative Extension Service map (*North Carolina Watersheds* by J. Fels published in 1997) (Figure 3) and Griffith, *et al*. (2002). More specifically, the Outer Piedmont includes:

- Cape Fear River Basin -- except for the streams draining the Sand Hills in Moore, Lee, and Harnett counties, the entire basin upstream of Lillington, NC;
- Neuse River Basin -- the entire basin above Smithfield and Wilson, NC, except for the south and southwest portions of Johnston County and the eastern two-thirds of Wilson County;
- Roanoke River Basin -- the entire basin in North Carolina upstream of Roanoke Rapids, NC and a small area between Roanoke Rapids and Halifax, NC; and
- Tar River Basin -- the entire basin above Rocky Mount, NC, except for the lower southeastern one-half of Halifax County and the extreme eastern portion of Nash County.

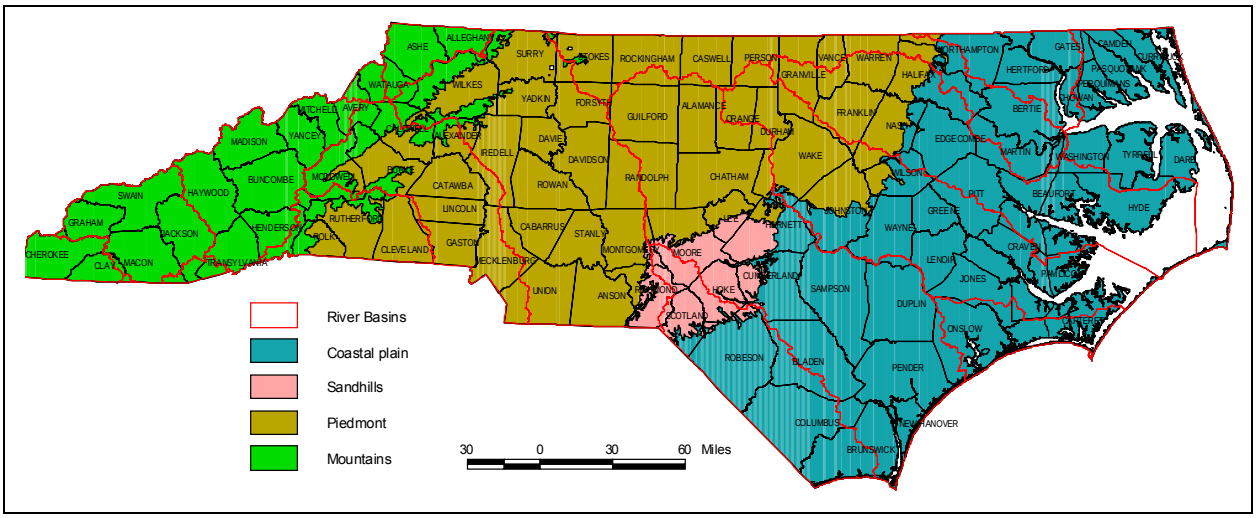

Figure 3. Physiographic regions and river basins in North Carolina.

The Index is undergoing revisions for the Upper Coastal Plain (Chowan, Neuse, Pasquotank, Roanoke, Tar, and White Oak River basins), the Lower Coastal Plain (Cape Fear and Lumber River basins), and the Sand Hills (Cape Fear, Lumber, and Yadkin River basins).

NCIBI QUALIFIERS

The North Carolina Index of Biological Integrity is only applicable if the methods of collection and data analyses described herein are strictly followed. The Index has not been tested using other collection techniques. Nonwadeable streams and larger rivers that must be sampled with a boat are not currently evaluated with the NCIBI. Neither are high elevation, cold water trout streams. Southern Appalachian trout streams are typically high gradient streams with plunge pools, *Rhododendron*- and Eastern hemlock-lined within a forested watershed, have cold water with low specific conductance, have a naturally low fish species diversity (usually brook trout, rainbow trout, or brown trout, blacknose dace, and mottled sculpin), have few tolerant fish, and support a reproducing population of one or more species of trout. Finally, young-of-year fish are excluded from all NCIBI calculations.

NCIBI ANALYSIS

The NCIBI incorporates information about species richness and composition, pollution indicator species, trophic composition, fish abundance, fish condition, and reproductive function by the cumulative assessment of 12 parameters or metrics (Tables 1 - 3). Each metric is designed to contribute unique information to the overall assessment. The values provided by the metrics are converted into scores on a 1, 3, and 5 scale. A score of 5 represents conditions commonly associated with undisturbed reference streams in the specific river basin or ecoregion. A score of 1, however, indicates that conditions deviate greatly from those typically observed in undisturbed streams of the region. All metrics for each of the three regions were calibrated using regional reference sites.

The scores for all metrics are then summed to obtain the overall NCIBI score, an even number between 12 and 60. The score is then used to determine the biological integrity class of the stream (i.e., Poor, Fair, Good-Fair, Good, or Excellent) (Karr 1981 , Karr, *et al.* 1986). A fish community rated Excellent is comparable to the best situations with minimal human disturbance; all regionally expected species for the habitat and stream size, including the most intolerant forms, are present along with a full array of size classes and a balanced trophic structure. Conversely, a fish community rated Poor deviates greatly from the reference condition. The number of fish is fewer than expected, usually fewer than expected number of species, an absence of intolerant species, and an altered trophic structure. Communities rated Good, Good-Fair, or Fair fall within this disturbance gradient.

Currently, if a fish community is rated Excellent, Good, or Good-Fair it is deemed to be Fully Supporting its Aquatic Life Use Support stream classification. If a fish community is rated Fair or Poor it is deemed to be Not Supporting its Life Use Support stream classification and the water quality standard is not being met. Waters that have an Excellent fish community rating are also eligible for reclassification to a Outstanding Resource Waters or to a High Quality Waters supplemental classifications.

NCIBI METRICS

These 12 metrics (Tables 1 – 3) are grouped into five categories with each metric designed to contribute unique information to the overall assessment:

1. Species richness and composition (Metric Nos. 1 and 3 - 5)
2. Indicator species (Metric Nos. 6 and 7)
3. Trophic function (Metric Nos. 8 - 10)
4. Abundance and condition (Metric Nos. 2 and 11)
5. Reproductive function (Metric No. 12)

Eight of the metrics involve species composition, pollution tolerance, and trophic composition. Table 4 lists, phylogenetically, the pollution tolerance ratings and trophic guild assignments of the freshwater fish found throughout North Carolina. Several of the species (for example, Paddlefish, American Shad, and Sauger) will not be encountered in streams that are sampled adhering to these procedures. Estuarine

species, extirpated species, and species found in nearby drainages of bordering states (but not in North Carolina) are not included. Revisions and updates to this table will be published periodically.

SPECIES RICHNESS AND COMPOSITION (Metric Nos. 1 and 3 - 5)
Distributional data for these four metrics were obtained from Menhinick (1991), Lee, *et al*. (1980), Biological Assessment Branch studies, North Carolina State Museum of Natural Sciences, Tennessee Valley Authority, and many other sources.

- **Metric No. 1. Number of Species**
  The total number of species supported by a stream of a given size in a given region decreases with environmental degradation. In addition, some streams with larger watersheds or drainage areas can be expected to support more species than streams with smaller watersheds. In other instances, the number of species and the watershed size are not correlated. This metric is rated according to the river basin from which the sample was taken and, in the case of the Inner Piedmont, Foothills, and Eastern Mountains region, the drainage area size at the sampling point. Drainage area size is calculated from USGS 7.5 minute series topographic maps or from the Division's geographic information system, if not otherwise known (ambient database, USGS publications, or a USGS masterfile printout which gives drainage areas for many streams at given road crossings). This metric is a count of all the species in the sample.

- **Metric No. 3. Number of Species of Darters**
  Darters are sensitive to environmental degradation particularly as a result of their specific reproductive and habitat requirements (Page 1983, Kuehne and Barbour 1983). Darter habitats are degraded as a result of channelization, siltation, and reduced oxygen levels. The collection of fewer than the expected number of species of darters can indicate that some degree of habitat degradation is occurring. This metric is a count of all the species of *Etheostoma* and *Percina* in the sample (Table 4).

  As with Metric No. 1, the total number of species of darters supported by a stream of a given size in a given region decreases with environmental degradation. In addition, some streams with larger watersheds or drainage areas can be expected to support more species than streams with smaller watersheds. In other instances, the number of species and the watershed size are not correlated. This metric is rated according to the river basin from which the sample was taken and, in the case of the Inner Piedmont, Foothills, and Eastern Mountains region, the drainage area size at the sampling point.

- **Metric No. 4. Number of Species of Rockbass, Smallmouth Bass, and Trout (Western and Northern Mountains)**
  Rock Bass, Smallmouth Bass, and the three species of trout are particularly responsive to habitat degradation such as the filling in of pools with sediment and the loss of instream cover. This metric is a count of these five species in the sample. Stocked trout (characterized by pale colors and worn or deformed fins) are not counted.

- **Metric No. 4 Number of Species of Sunfish, Bass, and Trout (Inner Piedmont, Foothills, and Eastern Mountains)**
  Sunfish, black bass, and trout species are particularly responsive to habitat degradation such as the filling in of pools with sediment and the loss of instream cover. This metric includes *Lepomis* (all species), *Centrarchus macropterus*, *Ambloplites rupestris*, *Pomoxis* (both species) *Micropterus* (all species), and all three species of trout (Table 4). Stocked trout (characterized by pale colors and worn or deformed fins) are not counted.

- **Metric No. 4 Number of Species of Sunfish (Outer Piedmont)**
  Sunfish species are particularly responsive to habitat degradation such as the filling in of pools with sediment and the loss of instream cover. This metric includes *Lepomis* (all species), *Enneacanthus* (all species), *Centrarchus macropterus*, *Acantharchus pomotis*, and *Ambloplites cavifrons* (Table 4).

- **Metric No. 5 Number of Species of Cyprinids (Western and Northern Mountains)**
  Many species of minnows are intolerant of habitat and chemical degradation and, because some of the species may have life spans up to six years, provide a multiyear integrated perspective. They also reflect the condition of the benthic community which may be harmed by sedimentation or by sediment contamination. In the Western and Northern Mountains, the Number of Species of Cyprinds (Minnows) is used as a substitute metric for the Number of Species of Suckers. This metric is a count of all the species within the family Cyprinidae in the sample (Table 4).

- **Metric No. 5. Number of Species of Suckers (Inner Piedmont, Foothills, and Eastern Mountains and Outer Piedmont)**
  Many species of suckers are intolerant of habitat and chemical degradation and, because they are long lived, provide a multiyear integrated perspective. They also reflect the condition of the benthic community which may be harmed by sedimentation or by sediment contamination. This metric is a count of all the species within the family Catostomidae in the sample (Table 4).

<u>INDICATOR SPECIES (Metric Nos. 6 and 7)</u>
The tolerance ratings for these two metrics were derived from Karr, *et al*. (1986), Saylor and Scott (1987), from polling various university, federal, and state fisheries management personnel using the Delphi Technique (Zuboy 1981), Etnier and Starnes (1993), Jenkins and Burkhead (1993), Rohde, *et al*. (1994), and from Biological Assessment Branch data.

- **Metric No. 6 Number of Intolerant Species**
  Intolerant species are those which are most affected by environmental perturbations and therefore should disappear, at least as viable populations, by the time a stream is rated as "Fair". Intolerant species also includes some species that have a very restricted zoogeographic distribution or are considered rare, endangered, or threatened. Of the approximately 219 species of freshwater fish found in North Carolina, 54 species are considered intolerant. This metric is a count of all intolerant species in the sample (Tables 4 and 5).

- **Metric No. 7 Percentage of Tolerant Individuals**
  Tolerant species are those which are often present in a stream in low or moderate numbers but as the stream degrades, they can become dominant. Of the approximately 219 species of freshwater fish found in North Carolina, 21 species (and one hybrid) are considered tolerant. This metric is a percentage metric. The number of individuals of the tolerant species (Tables 4 and 5) is summed and divided by the total number of fish collected to obtain the percentage of tolerant fish in the sample.

<u>TROPHIC FUNCTION (Metric Nos. 8 - 10)</u>
These three trophic composition metrics are used to measure the divergence from expected production and consumption patterns in the fish community that can result from environmental degradation. The main cause for a shift in the trophic composition of the fish community, generally a greater proportion of omnivores and lesser proportion of insectivores than what is expected, is nutrient enrichment. However, in some instances, the percentage of insectivores, especially Redbreast Sunfish *Lepomis auritus*, may increase dramatically due to environmental degradation and nutrient enrichment. And where the herbivorous Central Stoneroller *Campostoma anomalum* is found, canopy removal, riparian alteration, and nutrient enrichment may lead to its dramatic increase.

The trophic guild data for these three metrics were derived from the literature (Lee, *et al*. (1980), Karr, *et al*. (1986), Plafkin, *et al*. (1989), Etnier and Starnes (1993), Jenkins and Burkhead (1993), Rohde, *et al*. (1994)), and from Biological Assessment Branch data.

- **Metric No. 8 Percentage of Omnivorous + Herbivorous Individuals**
  This metric is a percentage metric. The number of individuals of omnivores and herbivores (Table 4) is summed and divided by the total number of fish collected.
- **Metric No. 9 Percentage of Insectivores**
  The number of individuals of insectivores (Table 4) is summed and divided by the total number of fish collected.

- **Metric No. 10 Percentage of Piscivores**
  The number of individuals of piscivores (Table 4) is summed and divided by the total number of fish collected. This metric was not used in the Western and Northern Mountains region because the metric failed to discriminate between the impaired and the reference sites and was not significantly correlated with the total NCIBI score. No substitute or alternative metrics were found suitable.

ABUNDANCE AND CONDITION (Metric Nos. 2 and 11)

- **Metric No. 2 Number of Fish**
  The total number of fish supported by a stream of a given size in a given region decreases with environmental degradation. However, in some instances, nutrient enrichment or environmental degradation may actually increase the number of fish supported by the stream. This metric is a count of all the fish in the sample.

- **Metric No. 11 The Percentage of Diseased Fish**
  This metric occurs infrequently, and in most instances, is absent entirely. The metric does occur below point sources and in areas where toxic chemicals are concentrated (e.g., Sanders, *et al.* 1999). This metric is: "*an excellent measure of the aesthetic value of game and nongame fish*" (Barbour, *et al.* 1999).

  DELT (Disease, fin Erosion, Lesions, and Tumors) may not be observed in streams the size of which are typically sampled because the worst (urban and industrial) streams are often not sampled. Neither are the larger streams and rivers where NPDES dischargers are typically located and which may have a greater DELT rate than the smaller streams. Generally, North Carolina fish are healthy.

  To rate this metric, the number of fish in the sample which have sores, lesions, skeletal anomalies (as evident externally), or diseased, damaged, or rotten fins is summed and divided by total number of fish collected to obtain the percentage of diseased fish. Fin or other external damage as a result of spawning should not be counted. Fish are considered to be in spawning condition when tubercles or breeding colors are evident.

  This metric was not used in the Western and Northern Mountains region because the metric failed to discriminate between the impaired and the reference sites and was not significantly correlated with the total NCIBI score. No substitute or alternative metrics were found suitable.

  Blackspot and Other Diseases
  Blackspot and yellow grub diseases are naturally occurring, common infections of fish by an immature stage of flukes. The life cycle involves fish, snails, and piscivorous birds. Although heavy, acute infections can be fatal, especially to small fish, fish can carry amazingly high worm burdens without any apparent ill effects (Noga 1996). Although some researchers incorporate the incidence of black spot and yellow grub into indices of biotic integrity (e.g., Steedman 1991), others, because of a lack of a consistent, inverse relationship to environmental quality, do not (e.g., Sanders, *et al*. 1999). The diseases are not considered in the NCIBI because it is widespread, affecting fish in all types of streams.

REPRODUCTIVE FUNCTION (Metric No. 12)

- **Metric No. 12 Percentage of Species with Multiple Age Groups**
  This metric was developed by the Division in 1989 as an indicator of the suitability of the habitat for reproduction. Other researchers have used proportion of individuals as hybrids, proportion of individuals as introduced species, simple lithophils (species of fish that spawn where the egg can develop in the interstices of sand, gravel, and cobble substrates without parental care), and number of simple lithophils (Barbour, *et al*. 1999). This metric is strongly influenced by rare species (species represented by 1 or 2 fish) that are not reproducing in the stream. A community may be diverse but if a large proportion of the species are represented by only 1 or 2 fish per species, these rarer species may depress the metric value.

For each species, the total length distribution data are used to determine the presence of different age groups and, thus, the degree of reproductive success. This metric is calculated by first counting the total number of species present in the sample. Then, the total lengths of all the fish of each species are examined to determine whether or not all the fish of that species are of one or multiple age groups. Finally, the percentage of species with multiple age groups is determined by dividing the number of species with multiple age groups by the total number of species collected in the sample. Although some species are rare and some species have fewer age groups than others, at least three individuals per species must have been collected to determine the presence of multiple age groups within the population. In some instances, professional judgment may also be used to determine the reproductive success of a particular species.

Publications such as Carlander (1969 and 1977), Kuehne and Barbour (1983), Page (1983), Manooch (1984), Etnier and Starnes (1993), Jenkins and Burkhead (1993), and Rohde, *et al*. (1994) may also be consulted to determine length-age class relationships.

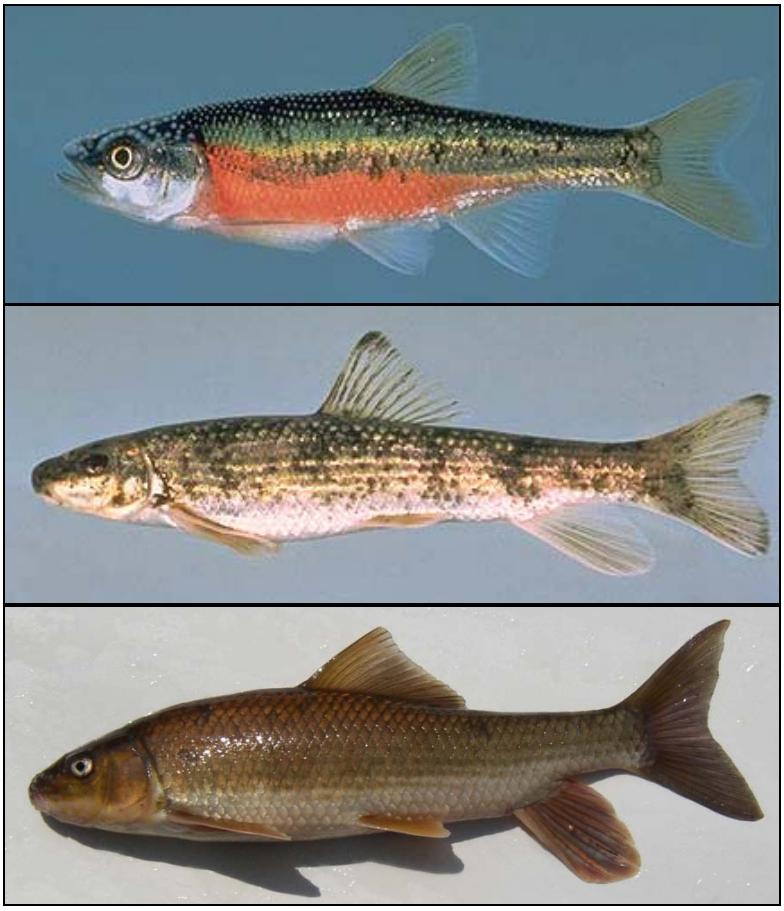

Table 1. Scoring criteria for the NCIBI for wadeable streams in the Western and Northern Mountains of the French Broad (including the Pigeon River), Hiwassee, Little Tennessee, New, and Watauga River basins with watersheds ranging between 3.1 and 161 mi^2.

No.	Metric		Score
1	**No. of species**		
	≥ 16 species		5
	12-15 species		3
	< 12 species		1
2	**No. of fish**		
	320-1,000 fish		5
	205-319 fish		3
	< 205 fish		1
	> 1,000 fish		3
3	**No. of species of darters**		
	French Broad & Little Tennessee River Basins	New River, Pigeon River, Watauga[1], & Hiwassee River Basins	
	≥ 4 species	≥ 3 species	5
	2 or 3 species	1 or 2 species	3
	0 or 1 species	0 species	1
4	**No. of species of Rock Bass, Smallmouth Bass, and trout**		
	≥ 2 species		5
	1 species		3
	0 species		1
5	**No. of species of cyprinids**		
	All basins, except Pigeon River Basin	Pigeon River Basin	
	≥ 8 species	≥ 6 species	5
	6 or 7 species	4 or 5 species	3
	≤ 5 species	≤ 3	1
6	**No. of intolerant species**		
	All basins, except New River Basin	New River Basin	
	≥ 3 species	≥ 5 species	5
	2 species	3 or 4 species	3
	0 or 1 species	0, 1, or 2 species	1
7	**Percentage of tolerant individuals**		
	≤ 2%		5
	2-10%		3
	> 10%		1
8	**Percentage of omnivorous + herbivorous individuals**		
	10-36%		5
	37-50%		3
	> 50%		1
	< 10%		1
9	**Percentage of insectivorous individuals**		
	55-85%		5
	40-54%		3
	< 40%		1
	> 85%		1
12	**Percentage of species with multiple age groups**		
	≥ 65% of all species have multiple age groups		5
	45-64% all species have multiple age groups		3
	< 45% all species have multiple age groups		1

[1]Tentative for the Watauga River basin; also includes *Cottus bairdi* (Mottled Sculpin) and *Noturus insignis* (Margined Madtom). The Watauga River Basin and the Toxaway River (Savannah River Basin) are the only river basins in North Carolina where these three benthic, insectivorous groups (darters, Mottled Sculpin, and Margined Madtom) are sympatric.

Table 2. Scoring criteria for the NCIBI for wadeable streams in the Inner Piedmont, Foothills, and Eastern Mountains of the Broad, Catawba, Savannah, and Yadkin River basins with watershed drainage areas ranging between 2.8 and 245 mi^2.

No.	Metric		Score
1	**No. of species**		
	where Y is the number of species in the sample and X is the stream's drainage area in mi^2:		
	$Y \geq 9.5*Log_{10}X+1.6$		5
	$4.8*Log_{10}X+0.8 \leq Y < 9.5*Log_{10}X+1.6$		3
	$Y < 4.8*Log_{10}X+0.8$		1
2	**No. of fish**		
	Mountains	Piedmont	
	≥ 300 fish	≥ 150 fish	5
	200-299 fish	100-149 fish	3
	< 200 fish	< 100 fish	1
3	**No. of species of darters**		
	where Y is the number of species of darters in the sample and X is the stream's drainage area in mi^2.		
	$Y \geq 1.6*Log_{10}X$		5
	$0.8*Log_{10}X \leq Y < 1.6*Log_{10}X$		3
	$Y < 0.8*Log_{10}X$		1
	If the drainage area is > 70 mi^2, then ≥ 3 species = 5, 2 species = 3, and 0 or 1 species = 1		
4	**No. of species of sunfish, bass, and trout**		
	≥ 3 species		5
	2 species		3
	0 or 1 species		1
5	**No. of species of suckers**		
	≥ 2 species		5
	1 species		3
	0 species		1
6	**No. of intolerant species**		
	Mountains	Piedmont	
	≥ 3 species	≥ 1 species	5
	1or 2 species	(no middle criteria or score)	3
	0 species	0 species	1
7	**Percentage of tolerant individuals**		
	Mountains	Piedmont	
	≤ 12%	≤ 25%	5
	13-25%	26-35%	3
	> 25%	> 35%	1
8	**Percentage of omnivorous + herbivorous individuals**		
	10-35%		5
	36-50%		3
	> 50%		1
	< 10%		1
9	**Percentage of insectivorous individuals**		
	60-90%		5
	45-59%		3
	< 45%		1
	> 90%		1
10	**Percentage of piscivorous individuals**		
	≥ 1.0%		5
	0.25-1.0%		3
	< 0.24%		1
11	**Percentage of diseased fish (DELT = diseased, fin erosion, lesions, and tumors)**		
	< 0.75%		5
	0.76-1.25%		3
	> 1.25%		1
12	**Percentage of species with multiple age groups**		
	Mountains	Piedmont	
	≥ 65% of all species have multiple age groups	≥ 55% of all species have multiple age groups	5
	45-64% all species have multiple age groups	35-54% all species have multiple age groups	3
	< 45% all species have multiple age groups	< 35% all species have multiple age groups	1

Table 3. Scoring criteria for the NCIBI for wadeable streams in the Outer Piedmont of the Cape Fear, Neuse, Roanoke, and Tar River basins ranging between 3.1 and 328 mi^2.

No.	Metric		Score
1	**No. of species**		
	≥ 16 species		5
	10-15 species		3
	< 10 species		1
2	**No. of fish**		
	≥ 225 fish		5
	150-224 fish		3
	< 150 fish		1
3	**No. of species of darters**		
	Cape Fear	Neuse, Roanoke, and Tar	
	≥ 2 species	≥ 3 species	5
	1 species	1 or 2 species	3
	0 species	0 species	1
4	**No. of species of sunfish**		
	≥ 4 species		5
	3 species		3
	0, 1, or 2 species		1
5	**No. of species of suckers**		
	Cape Fear	Neuse, Roanoke, and Tar	
	≥ 2 species	≥ 3 species	5
	1 species	1 or 2 species	3
	0 species	0 species	1
6	**No. of intolerant species**		
	Cape Fear	Neuse, Roanoke, and Tar	
	≥ 1 species	≥ 3 species	5
	no middle score	1 or 2 species	3
	0 species	0 species	1
7	**Percentage of tolerant individuals**		
	≤ 35%		5
	36-50%		3
	> 50%		1
8	**Percentage of omnivorous and herbivorous individuals**		
	10-35%		5
	36-50%		3
	> 50%		1
	< 10%		1
9	**Percentage of insectivorous individuals**		
	65-90%		5
	45-64%		3
	< 45%		1
	> 90%		1
10	**Percentage of piscivorous individuals**		
	≥ 1.4-15%		5
	0.4-1.3%		3
	< 0.4%		1
	> 15%		1
11	**Percentage of diseased fish (DELT = diseased, fin erosion, lesions, and tumors)**		
	≤ 1.75%		5
	1.76-2.75%		3
	> 2.75%		1
12	**Percentage of species with multiple age groups**		
	≥ 50% of all species have multiple age groups		5
	35-49% all species have multiple age groups		3
	< 35% all species have multiple age groups		1

Table 4. North Carolina freshwater fishes tolerance ratings, adult trophic guild assignments, and young-of-year (YOY) cut-off lengths (total length in millimeters). Common and scientific names follow Nelson, *et al*. (2004), except for *Scartomyzon*.

Family/ Species	Common Name	Tolerance Rating	Trophic Guild of Adults	YOY (< TL mm)
Petromyzontidae	**Lampreys**			
Ichthyomyzon bdellium	Ohio Lamprey	Intermediate	Parasitic	50
I. castaneus	Chestnut Lamprey	Intermediate	Parasitic	
I. greeleyi	Mountain Brook Lamprey	Intermediate	Non-feeding	40
Lampetra aepyptera	Least Brook Lamprey	Intolerant	Non-feeding	50
L. appendix	American Brook Lamprey	Intermediate	Non-feeding	40
Petromyzon marinus	Sea Lamprey	Intermediate	Parasitic	100
Acipenseridae	**Sturgeons**			
Acipenser brevirostrum	Shortnose Sturgeon	Intermediate	Insectivore	200
A. oxyrinchus	Atlantic Sturgeon	Intermediate	Insectivore	200
Polyodontidae	**Paddlefishes**			
Polyodon spathula	Paddlefish	Intermediate	Planktivore	200
Lepisosteidae	**Gars**			
Lepisosteus osseus	Longnose Gar	Tolerant	Piscivore	200
Amiidae	**Bowfins**			
Amia calva	Bowfin	Tolerant	Piscivore	200
Hiodontidae	**Mooneyes**			
Hiodon tergisus	Mooneye	Intermediate	Insectivore	100
Anguillidae	**Freshwater Eels**			
Anguilla rostrata	American Eel	Intermediate	Piscivore	100
Clupeidae	**Herrings and Shads**			
Alosa aestivalis	Blueback Herring	Intermediate	Insectivore	100
A. mediocris	Hickory Shad	Intermediate	Insectivore	100
A. pseudoharengus	Alewife	Intermediate	Insectivore	50
A. sapidissima	American Shad	Intermediate	Insectivore	100
Dorosoma cepedianum	Gizzard Shad	Intermediate	Omnivore	100
D. petenense	Threadfin Shad	Intermediate	Omnivore	100
Cyprinidae	**Carps and Minnows**			
Campostoma anomalum	Stoneroller	Intermediate	Herbivore	60
Carassius auratus	Goldfish	Tolerant	Omnivore	50
Clinostomus funduloides	Rosyside Dace	Intermediate	Insectivore	40
Ctenopharyngodon idella	Grass Carp	Tolerant	Herbivore	200
Cyprinella analostana	Satinfin Shiner	Tolerant	Insectivore	40
C. chloristia	Greenfin Shiner	Intermediate	Insectivore	40
C. galactura	Whitetail Shiner	Intermediate	Insectivore	50
C. labrosa	Thicklip Chub	Intolerant	Insectivore	40
C. lutrensis	Red Shiner	Tolerant	Insectivore	30
C. nivea	Whitefin Shiner	Intermediate	Insectivore	40
C. pyrrhomelas	Fieryblack Shiner	Intolerant	Insectivore	40
C. spiloptera	Spotfin Shiner	Intermediate	Insectivore	40
C. zanema	Santee Chub	Intolerant	Insectivore	40
C. sp. cf. *zanema*	"Thinlip" Chub	Intolerant	Insectivore	40
Cyprinus carpio	Common Carp	Tolerant	Omnivore	150
Erimonax monachus	Spotfin Chub	Intolerant	Insectivore	40
Erimystax insignis	Blotched Chub	Intermediate	Omnivore	40
Exoglossum laurae	Tonguetied Minnow	Intolerant	Insectivore	50
E. maxillingua	Cutlip Minnow	Intolerant	Insectivore	50
Hybognathus regius	Eastern Silvery Minnow	Intermediate	Herbivore	50
Hybopsis amblops	Bigeye Chub	Intermediate	Insectivore	50
H. hypsinotus	Highback Chub	Intolerant	Insectivore	40
H. rubifrons	Rosyface Chub	Intolerant	Insectivore	50
Luxilus albeolus	White Shiner	Intermediate	Insectivore	50
L. cerasinus	Crescent Shiner	Intermediate	Insectivore	50
L. chrysocephalus	Striped Shiner	Intermediate	Omnivore	50
L. coccogenis	Warpaint Shiner	Intermediate	Insectivore	50

Table 4 (continued).

Family/ Species	Common Name	Tolerance Rating	Trophic Guild of Adults	YOY (< TL mm)
Lythrurus ardens	Rosefin Shiner	Intermediate	Insectivore	50
L. matutinus	Pinewoods Shiner	Intolerant	Insectivore	50
Nocomis leptocephalus	Bluehead Chub	Intermediate	Omnivore	50
N. micropogon	River Chub	Intermediate	Omnivore	50
N. platyrhynchus	Bigmouth Chub	Intermediate	Omnivore	50
N. raneyi	Bull Chub	Intermediate	Omnivore	50
Notemigonus crysoleucas	Golden Shiner	Tolerant	Omnivore	75
Notropis alborus	Whitemouth Shiner	Intermediate	Insectivore	40
N. altipinnis	Highfin Shiner	Intermediate	Insectivore	40
N. amoenus	Comely Shiner	Intermediate	Insectivore	50
N. bifrenatus	Bridle Shiner	Intermediate	Omnivore	40
N. chalybaeus	Ironcolor Shiner	Intolerant	Insectivore	40
N. chiliticus	Redlip Shiner	Intermediate	Insectivore	40
N. chlorocephalus	Greenhead Shiner	Intermediate	Insectivore	40
N. cummingsae	Dusky Shiner	Intermediate	Insectivore	40
N. hudsonius	Spottail Shiner	Intermediate	Omnivore	50
N. leuciodus	Tennessee Shiner	Intermediate	Insectivore	50
N. lutipinnis	Yellowfin Shiner	Intermediate	Insectivore	40
N. maculatus	Taillight Shiner	Intolerant	Insectivore	40
N. mekistocholas	Cape Fear Shiner	Intermediate	Omnivore	40
N. micropteryx	Highland Shiner	Intolerant	Insectivore	40
N. petersoni	Coastal Shiner	Intermediate	Insectivore	40
N. photogenis	Silver Shiner	Intolerant	Insectivore	50
N. procne	Swallowtail Shiner	Intermediate	Insectivore	40
N. rubricroceus	Saffron Shiner	Intermediate	Insectivore	40
N. scabriceps	New River Shiner	Intolerant	Insectivore	40
N. scepticus	Sandbar Shiner	Intermediate	Insectivore	40
N. spectrunculus	Mirror Shiner	Intermediate	Insectivore	40
N. telescopus	Telescope Shiner	Intolerant	Insectivore	40
N. volucellus	Mimic Shiner	Intolerant	Insectivore	40
N. sp. cf. *chlorocephalus*	"Piedmont" Shiner	Intermediate	Insectivore	40
N. sp. cf. *rubellus*	"Rosyface" Shiner	Intolerant	Insectivore	40
Phenacobius crassilabrum	Fatlips Minnow	Intermediate	Insectivore	50
P. teretulus	Kanawha Minnow	Intolerant	Insectivore	50
Phoxinus oreas	Mountain Redbelly Dace	Intermediate	Herbivore	40
Pimephales notatus	Bluntnose Minnow	Tolerant	Omnivore	30
P. promelas	Fathead Minnow	Tolerant	Omnivore	30
Rhinichthys cataractae	Longnose Dace	Intermediate	Insectivore	50
R. obtusus	Western Blacknose Dace	Intermediate	Insectivore	50
Semotilus atromaculatus	Creek Chub	Tolerant	Insectivore	50
S. lumbee	Sandhills Chub	Intolerant	Insectivore	40
Catostomidae	**Suckers**			
Carpiodes carpio	River Carpsucker	Intermediate	Omnivore	100
C. cyprinus	Quillback	Intermediate	Omnivore	100
C. velifer	Highfin Carpsucker	Intermediate	Omnivore	100
C. sp. cf. *cyprinus*	(no common name)	Intermediate	Omnivore	100
C. sp. cf. *velifer*	(no common name)	Intermediate	Omnivore	100
Catostomus commersonii	White Sucker	Tolerant	Omnivore	100
Erimyzon oblongus	Creek Chubsucker	Intermediate	Omnivore	100
E. sucetta	Lake Chubsucker	Intermediate	Insectivore	100
Hypentelium nigricans	Northern Hog Sucker	Intermediate	Insectivore	100
H. roanokense	Roanoke Hog Sucker	Intermediate	Insectivore	100
Ictiobus bubalus	Smallmouth Buffalo	Intermediate	Omnivore	100
I. cyprinellus	Bigmouth Buffalo	Intermediate	Insectivore	100
I. niger	Black Buffalo	Intermediate	Insectivore	100
Minytrema melanops	Spotted Sucker	Intermediate	Insectivore	100
Moxostoma anisurum	Silver Redhorse	Intermediate	Insectivore	100
M. breviceps	Smallmouth Redhorse	Intermediate	Insectivore	100
M. collapsum	Notchlip Redhorse	Intermediate	Insectivore	100
M. carinatum	River Redhorse	Intermediate	Insectivore	100
M. duquesnei	Black Redhorse	Intermediate	Insectivore	100
M. erythrurum	Golden Redhorse	Intermediate	Insectivore	100
M. macrolepidotum	Shorthead Redhorse	Intermediate	Insectivore	100
M. pappillosum	V-Lip Redhorse	Intermediate	Insectivore	100

Table 4 (continued).

Family/ Species	Common Name	Tolerance Rating	Trophic Guild of Adults	YOY (< TL mm)
M. robustum	Robust Redhorse	Intolerant	Insectivore	100
M. sp. cf. *erythrurum*	Carolina Redhorse	Intermediate	Insectivore	100
M. sp. cf. *macrolepidotum*	Sicklefin Redhorse	Intermediate	Insectivore	100
Scartomyzon ariommus	Bigeye Jumprock	Intolerant	Insectivore	100
S. cervinum	Blacktip Jumprock	Intermediate	Insectivore	75
S. rupiscartes	Striped Jumprock	Intermediate	Insectivore	100
S. sp. cf. *lachneri*	"Brassy" Jumprock	Intermediate	Insectivore	100
Thoburnia hamiltoni	Rustyside Sucker	Intolerant	Insectivore	
Ictaluridae	**North American Catfishes**			
Ameiurus brunneus	Snail Bullhead	Intermediate	Insectivore	75
A. catus	White Catfish	Tolerant	Omnivore	100
A. melas	Black Bullhead	Tolerant	Insectivore	75
A. natalis	Yellow Bullhead	Tolerant	Omnivore	75
A. nebulosus	Brown Bullhead	Tolerant	Omnivore	75
A. platycephalus	Flat Bullhead	Tolerant	Insectivore	75
Ictalurus furcatus	Blue Catfish	Intermediate	Piscivore	100
I. punctatus	Channel Catfish	Intermediate	Omnivore	100
Noturus eleutherus	Mountain Madtom	Intermediate	Insectivore	40
N. flavus	Stonecat	Intermediate	Insectivore	40
N. furiosus	Carolina Madtom	Intolerant	Insectivore	40
N. gilberti	Orangefin Madtom	Intolerant	Insectivore	40
N. gyrinus	Tadpole Madtom	Intermediate	Insectivore	40
N. insignis	Margined Madtom	Intermediate	Insectivore	40
N. sp. cf. *leptacanthus*	Broadtail Madtom	Intolerant	Insectivore	40
Pylodictis olivaris	Flathead Catfish	Intermediate	Piscivore	150
Esocidae	**Pikes**			
Esox americanus americanus	Redfin Pickerel	Intermediate	Piscivore	100
E. masquinongy	Muskellunge	Intermediate	Piscivore	200
E. niger	Chain Pickerel	Intermediate	Piscivore	100
Umbridae	**Mudminows**			
Umbra pygmaea	Eastern Mudminnow	Intermediate	Insectivore	50
Salmonidae	**Trouts and Salmons**			
Oncorhynchus mykiss	Rainbow Trout	Intolerant	Insectivore	100
Salmo trutta	Brown Trout	Intermediate	Piscivore	100
Salvelinus fontinalis	Brook Trout	Intolerant	Insectivore	100
Aphredoderidae	**Pirate Perches**			
Aphredoderus sayanus	Pirate Perch	Intermediate	Insectivore	50
Amblyopsidae	**Cavefishes**			
Chologaster cornuta	Swampfish	Intermediate	Insectivore	25
Atherinopsidae	**New World Silversides**			
Labidesthes sicculus	Brook Silverside	Intermediate	Insectivore	50
L. vanhyningi	Southern Brook Silverside	Intermediate	Insectivore	50
Menidia beryllina	Inland Silverside	Intermediate	Insectivore	50
M. extensa	Waccamaw Silverside	Intolerant	Insectivore	50
Fundulidae	**Topminnows**			
Fundulus chrysotus	Golden Topminnow	Intermediate	Insectivore	40
F. diaphanus	Banded Killifish	Intermediate	Insectivore	40
F. lineolatus	Lined Topminnow	Intermediate	Insectivore	40
F. rathbuni	Speckled Killifish	Intermediate	Insectivore	40
F. waccamensis	Waccamaw Killifish	Intolerant	Insectivore	40
Lucania goodei	Bluefin Killifish	Tolerant	Omnivore	15
Poeciliidae	**Livebearers**			
Gambusia affinis	Western Mosquitofish	Tolerant	Insectivore	20
G. holbrooki	Eastern Mosquitofish	Tolerant	Insectivore	20
Heterandria formosa	Least Killifish	Tolerant	Omnivore	10

Table 4 (continued).

Family/ Species	Common Name	Tolerance Rating	Trophic Guild of Adults	YOY (< TL mm)
Cottidae	**Sculpins**			
Cottus bairdii	Mottled Sculpin	Intermediate	Insectivore	50
C. carolinae	Banded Sculpin	Intermediate	Insectivore	50
C. caeruleomentum	Blue Ridge Sculpin	Intermediate	Insectivore	50
Moronidae	**Temperate Basses**			
Morone americana	White Perch	Intermediate	Piscivore	75
M. chrysops	White Bass	Intermediate	Piscivore	200
M. saxatilis	Striped Bass	Intermediate	Piscivore	175
Centrarchidae	**Sunfishes**			
Acantharchus pomotis	Mud Sunfish	Intermediate	Insectivore	50
Ambloplites cavifrons	Roanoke Bass	Intermediate	Piscivore	50
A. rupestris	Rock Bass	Intolerant	Piscivore	50
Centrarchus macropterus	Flier	Intermediate	Insectivore	50
Enneacanthus chaetodon	Blackbanded Sunfish	Intermediate	Insectivore	40
E. gloriosus	Bluespotted Sunfish	Intermediate	Insectivore	40
E. obesus	Banded Sunfish	Intermediate	Insectivore	40
Lepomis auritus	Redbreast Sunfish	Tolerant	Insectivore	50
L. cyanellus	Green Sunfish	Tolerant	Insectivore	50
L. gibbosus	Pumpkinseed	Intermediate	Insectivore	50
L. gulosus	Warmouth	Intermediate	Insectivore	50
L. macrochirus	Bluegill	Intermediate	Insectivore	50
L. marginatus	Dollar Sunfish	Intermediate	Insectivore	50
L. microlophus	Redear Sunfish	Intermediate	Insectivore	50
L. punctatus	Spotted Sunfish	Intermediate	Insectivore	50
Lepomis sp.	Hybrid Sunfish	Tolerant	Insectivore	50
Micropterus coosae	Redeye Bass	Intermediate	Piscivore	100
M. dolomieu	Smallmouth Bass	Intolerant	Piscivore	100
M. punctulatus	Spotted Bass	Intermediate	Piscivore	100
M. salmoides	Largemouth Bass	Intermediate	Piscivore	100
Pomoxis annularis	White Crappie	Intermediate	Piscivore	75
P. nigromaculatus	Black Crappie	Intermediate	Piscivore	75
Percidae	**Perches**			
Etheostoma acuticeps	Sharphead Darter	Intolerant	Insectivore	40
E. blennioides	Greenside Darter	Intermediate	Insectivore	40
E. brevispinum	Carolina Fantail Darter	Intermediate	Insectivore	30
E. chlorobranchium	Greenfin Darter	Intolerant	Insectivore	40
E. collis	Carolina Darter	Intermediate	Insectivore	30
E. flabellare	Fantail Darter	Intermediate	Insectivore	30
E. fusiforme	Swamp Darter	Intermediate	Insectivore	30
E. gutselli	Tuckasegee Darter	Intermediate	Insectivore	40
E. inscriptum	Turquoise Darter	Intolerant	Insectivore	40
E. jessiae	Blueside Darter	Intolerant	Insectivore	40
E. kanawhae	Kanawha Darter	Intolerant	Insectivore	40
E. mariae	Pinewoods Darter	Intolerant	Insectivore	30
E. nigrum	Johnny Darter	Intermediate	Insectivore	30
E. olmstedi	Tessellated Darter	Intermediate	Insectivore	40
E. perlongum	Waccamaw Darter	Intolerant	Insectivore	30
E. podostemone	Riverweed Darter	Intolerant	Insectivore	30
E. rufilineatum	Redline Darter	Intermediate	Insectivore	40
E. serrifer	Sawcheek Darter	Intolerant	Insectivore	30
E. swannanoa	Swannanoa Darter	Intermediate	Insectivore	40
E. thalassinum	Seagreen Darter	Intolerant	Insectivore	40
E. vitreum	Glassy Darter	Intermediate	Insectivore	30
E. vulneratum	Wounded Darter	Intolerant	Insectivore	40
E. zonale	Banded Darter	Intermediate	Insectivore	40
Perca flavescens	Yellow Perch	Intermediate	Piscivore	80
Percina aurantiaca	Tangerine Darter	Intolerant	Insectivore	40
P. burtoni	Blotchside Logperch	Intolerant	Insectivore	40
P. caprodes	Logperch	Intermediate	Insectivore	40
P. crassa	Piedmont Darter	Intolerant	Insectivore	40
P. evides	Gilt Darter	Intolerant	Insectivore	40
P. gymnocephala	Appalachia Darter	Intolerant	Insectivore	40

Table 4 (continued).

Family/ Species	Common Name	Tolerance Rating	Trophic Guild of Adults	YOY (< TL mm)
P. nevisense	Chainback Darter	Intolerant	Insectivore	40
P. nigrofasciata	Blackbanded Darter	Intolerant	Insectivore	40
P. oxyrhynchus	Sharpnose Darter	Intolerant	Insectivore	40
P. rex	Roanoke Logperch	Intolerant	Insectivore	40
P. roanoka	Roanoke Darter	Intolerant	Insectivore	30
P. squamata	Olive Darter	Intolerant	Insectivore	
Sander canadensis	Sauger	Intermediate	Piscivore	
S. vitreus	Walleye	Intermediate	Piscivore	
Elassomatidae	**Pygmy Sunfishes**			
Elassoma evergladei	Everglades Pygmy Sunfish	Intermediate	Insectivore	20
E. zonatum	Banded Pygmy Sunfish	Intermediate	Insectivore	20
E. boehlkei	Carolina Pygmy Sunfish	Intolerant	Insectivore	20
Sciaenidae	**Drums**			
Aplodinotus grunniens	Freshwater Drum	Intermediate	Insectivore	

Table 5. Intolerant species of fish found in North Carolina.

Family/Species	Common Name	Family/Species	Common Name
Petromyzontidae	**Lampreys**	**Atherinopsidae**	**New World Silversides**
Lampetra aepyptera	Least Brook Lamprey	*Menidia extensa*	Waccamaw Silverside
Cyprinidae	**Carps and Minnows**	**Fundulidae**	**Topminnows**
Cyprinella labrosa	Thicklip Chub	*Fundulus waccamensis*	Waccamaw Killifish
C. pyrrhomelas	Fieryblack Shiner		
C. zanema	Santee Chub	**Centrarchidae**	**Sunfishes**
Erimonax monachus	Spotfin Chub	*Ambloplites rupestris*	Rock Bass
Exoglossum laurae	Tonguetied Minnow	*Micropterus dolomieu*	Smallmouth Bass
E. maxillingua	Cutlip Minnow		
Hybopsis hypsinotus	Highback Chub	**Percidae**	**Perches**
H. rubifrons	Rosyface Chub	*Etheostoma acuticeps*	Sharphead Darter
Lythrurus matutinus	Pinewoods Shiner	*E. chlorobranchium*	Greenfin Darter
Notropis chalybaeus	Ironcolor Shiner	*E. inscriptum*	Turquoise Darter
N. maculatus	Taillight Shiner	*E. jessiae*	Blueside Darter
N. micropteryx	Highland Shiner	*E. kanawhae*	Kanawha Darter
N. photogenis	Silver Shiner	*E. mariae*	Pinewoods Darter
N. scabriceps	New River Shiner	*E. perlongum*	Waccamaw Darter
N. telescopus	Telescope Shiner	*E. podostemone*	Riverweed Darter
N. volucellus	Mimic Shiner	*E. serrifer*	Sawcheek Darter
N. sp. cf. *rubellus*	Rosyface Shiner	*E. thalassinum*	Seagreen Darter
Phenacobius teretulus	Kanawha Minnow	*E. vulneratum*	Wounded Darter
Semotilus lumbee	Sandhills Chub	*Percina aurantiaca*	Tangerine Darter
		P. burtoni	Blotchside Logperch
Catostomidae	**Suckers**	*P. crassa*	Piedmont Darter
Moxostoma robustum	Robust Redhorse	*P. evides*	Gilt Darter
Scartomyzon ariommus	Bigeye Jumprock	*P. gymnocephala*	Appalachia Darter
Thoburnia hamiltoni	Rustyside Sucker	*P. nigrofasciata*	Blackbanded Darter
		P. nevisense	Chainback Darter
Ictaluridae	**North American Catfishes**	*P. oxyrhynchus*	Sharpnose Darter
Noturus furiosus	Carolina Madtom	*P. rex*	Roanoke Logperch
N. gilberti	Orangefin Madtom	*P. roanoka*	Roanoke Darter
N. sp. cf. *leptacanthus*	Broadtail Madtom	*P. squamata*	Olive Darter
Salmonidae	**Trouts and Salmons**	**Elassomatidae**	**Pygmy Sunfishes**
Oncorhynchus mykiss	Rainbow Trout	*Elassoma boehlkei*	Carolina Pygmy Sunfish
Salvelinus fontinalis	Brook Trout		

Table 6. Tolerant species of fish found in North Carolina.

Family/Species	Common Name	Family/Species	Common Name
Lepisosteidae	**Gars**	**Catostomidae**	**Suckers**
Lepisosteus osseus	Longnose Gar	*Catostomus commersonii*	White Sucker
Amiidae	**Bowfins**	**Ictaluridae**	**North American Catfishes**
Amia calva	Bowfin	*Ameiurus catus*	White Catfish
		A. melas	Black Bullhead
Cyprinidae	**Carps and Minnows**	*A. natalis*	Yellow Bullhead
Carassius auratus	Goldfish	*A. nebulosus*	Brown Bullhead
Ctenopharyngodon idella	Grass Carp	*A. platycephalus*	Flat Bullhead
Cyprinella analostana	Satinfin Shiner		
C. lutrensis	Red Shiner	**Poeciliidae**	**Livebearers**
Cyprinus carpio	Common Carp	*Gambusia affinis*	Western Mosquitofish
Notemigonus crysoleucas	Golden Shiner	*G. holbrooki*	Eastern Mosquitofish
Pimephales notatus	Bluntnose Minnow		
P. promelas	Fathead Minnow	**Centrarchidae**	**Sunfishes**
Semotilus atromaculatus	Creek Chub	*Lepomis auritus*	Redbreast Sunfish
		L. cyanellus	Green Sunfish
		Lepomis sp.	Hybrid Sunfish

INTEGRITY CLASS ASSIGNMENT

The scores for all 10 or 12 metrics are then summed to obtain the overall NCIBI score. Finally, the score (an even number between 12 and 60) is then used to determine the biological integrity class of the stream from which the sample was collected (Table 7).[1]

Table 7. Revised scores and classes for evaluating the fish community of a wadeable stream in select streams using the North Carolina Index of Biological Integrity.

River Basin	NCIBI Score	Integrity Class
French Broad, Hiwassee, Little Tennessee, New, and Watauga	58 or 60	Excellent
	48, 50, 52, 54, or 56	Good
	40, 42, 44, or 46	Good-Fair
	34, 36, or 38	Fair
	≤ 32	Poor
Broad, Catawba, Savannah, and Yadkin	54, 56, 58, or 60	Excellent
	48, 50, or 52	Good
	42, 44, or 46	Good-Fair
	36, 38, or 40	Fair
	≤ 34	Poor
Cape Fear, Neuse, Roanoke, and Tar	54, 56, 58, or 60	Excellent
	46, 48, 50, or 52	Good
	40, 42, or 44	Good-Fair
	34, 36, or 38	Fair
	≤ 32	Poor

[1] In the Western and Northern Mountains (French Broad, Hiwassee, Little Tennessee, New, and Watauga River basins), the NCIBI is based upon 10 rather than 12 metrics (Table 1). Using 10 metrics with each metric's criteria scored a 1, 3, or 5 and desiring to keep 60 as the maximum NCIBI Total Score, the total score was multiplied by 1.2 (60/50=1.2). Scores were rounded up or down to the nearest whole even number (e.g., 57.6 rounded up to 58; 50.4 rounded down to 50). Using 10 metrics instead of 12 and following the conversions as described, the final Total NCIBI Scores of 54, 42, 30, and 18 are no longer possible. This slight flaw should not affect the usefulness and applicability of the 10 metric NCIBI for the Western and Northern Mountains

Total Score based upon 10 Metrics before Multiplier	Total Score based upon 10 Metrics after Applying a 1.2 Multiplier	Final Total Score after Rounding (if necessary)
50	60	60
48	57.6	58
46	55.2	56
44	52.8	52
42	50.4	50
40	48	48
38	45.6	46
36	43.2	44
34	40.8	40
32	38.4	38
30	36	36
28	33.6	34
26	31.2	32
24	28.8	28
22	26.4	26
20	24	24
18	21.6	22
16	19.2	20
14	16.8	16
12	14.4	14

OTHER WATER QUALITY INDICATORS

Although the North Carolina Index of Biological Integrity is the primary tool used in the Stream Fish Community Assessment Program, other water quality measurements (e.g., water temperature, dissolved oxygen, pH, specific conductance, and water clarity are also monitored at every site in accordance with the Intensive Survey Branch's SOP (NCDENR 2011). At each site, a non-regulatory stream and riparian habitat assessment is conducted (Appendices 5 and 6).

FIELD SAMPLING AND LABORATORY PROCESSING METHODS

SAMPLING SCHEDULE AND FREQUENCY

Sites that are part of the Basinwide Monitoring Program are sampled once every five years and, due to staffing constraints, usually between April and June. For example, basinwide sites in the Yadkin River Basin were sampled in 1996, 2001, 2006, 2011, and will be sampled again in 2016 (Figure 4). Watershed-specific special study sites that are designed to address a specific, short-term question (e.g., Use Attainability, impacts from a permitted discharger, watershed modifications, *etc*.) are usually sampled only once and may be sampled anytime between March and December.

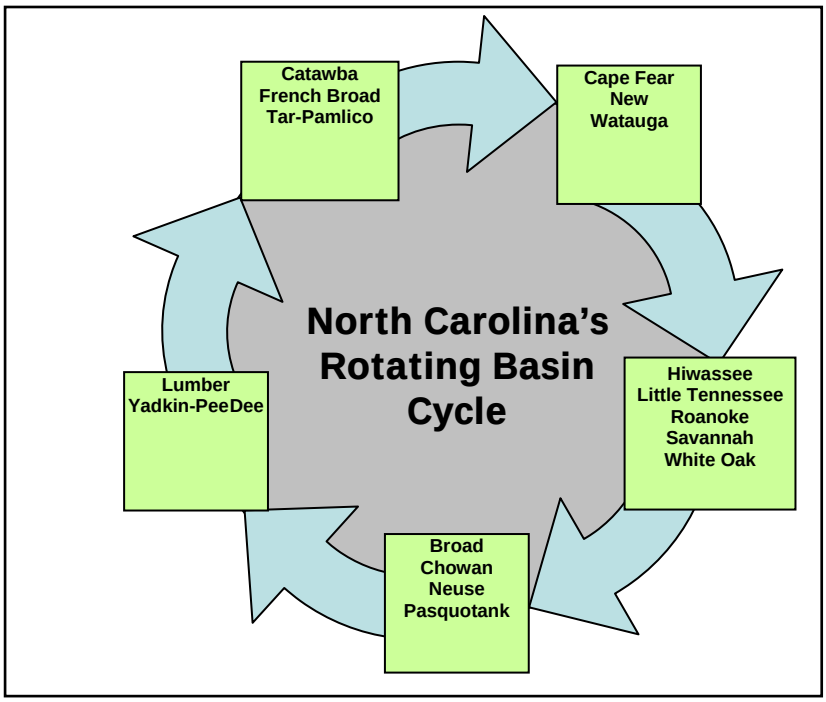

Figure 4 **North Carolina's rotating basinwide planning schedule for its 17 river basins. Individual Basins are grouped (as indicated by the green boxes) and assessed on a 5-year rotating cycle.**

FISH COLLECTION LICENSES AND PERMITS

Collection permits are required to collect fish from North Carolina freshwater ecosystems and must accompany the field staff whenever collections are made. Annually, it is the responsibility of the Sr. Environmental Specialist to insure that a Scientific Collection License and an Endangered Species Permit have been obtained from the North Carolina Wildlife Resources Commission's Division of Boating and Inland Fisheries and from the Division of Wildlife Management.

SITE LOCATIONS

Sites are established at publicly accessible, fixed locations (i.e., specific latitude and longitude), generally at bridge crossings. Lists of all the sites ever monitored, by river basin, may be found at: http://portal.ncdenr.org/web/wq/ess/bau/ncibi-data. Locations and their geo-references were originally

identified using USGS 7.5 minute topographic maps or Maptech Terrain Navigator ® software. Stations are strategically located to monitor a specific area of concern such as:

- overall water quality in a larger watershed,
- effect of point source discharges,
- effect of non-point sources of pollution (e.g., urban areas, animal operations, agriculture),
- effect of land use changes,
- waters of significant ecological, recreational, political, or municipal use, or
- waters that show an impairment due to unknown causes.

Sites that have been monitored between 1991 and 2012 were previously shown in Figure 2. Because this is a relatively new program, many of the current sites have been active for only 1 to 3 basinwide monitoring cycles. However, maintenance of many of these sites on a long-term basis is integral to identifying temporal patterns within a watershed and to gaining an understanding of the variability within the fish community. Consequently, requests from DWR staff for station establishment and/or discontinuation will be assessed on the value gained from a long-term perspective. Requests for additional sampling of sites (usually a one-time sampling event within a watershed) are handled through special studies. Adjustments to site locations and sampling regimens may be made with sufficient reason, such as:

- safety concerns of field staff,
- changes to location accessibility,
- the reason for sampling is no longer valid (i.e., a discontinued discharge),
- the emergence of new water quality concerns, or
- resource constraints, particularly staff vacancies.

If any of these concerns arise, the Sr. Environmental Specialist will meet with the BAB Supervisor to determine if it is appropriate for the site to be discontinued.

Sampling condition limitations are dictated by extremes in water clarity (turbidity), stream width and depth (too wide and deep), substrate (deep muck), precipitation (rainfall and electrical storms), aquatic macrophyte growths (excessive), flow (not flowing or too much flow), dangerous sampling conditions, time of day (lateness in the afternoon), *etc*.

A representative wadeable site of approximately 600 ft. is selected. Wadeable streams are those that can be safely waded by the sampling crew while wearing a backpack electrofisher unit and still allow the sampler and netter to reach all areas of the stream with the electrofishing probes and dipnet. When possible, the delineated reach should be located upstream from the bridge access area. If possible, personnel measuring the stream segment should avoid walking in the stream segment to avoid scaring fish out of the sample segment and to minimize habitat disturbance.

FIELD VARIABLES

The Stream Fish Community Assessment Program Samples Log Sheet (Appendix 1) is updated and a Stream Fish Community Assessment Program Field Data Sheet (Appendix 2) is completed whenever a sample is collected. Data that are recorded include: stream name, sample location, county, river basin, subbasin, latitude, longitude, drainage area, stream index number and classification (obtained from Basinwide Information Management System), habitat score, elevation, sample number, sample date, time, number of shocking units, duration of shocking, sampling personnel, location of sample reach, and use of a seine (yes or no). An example of a completed sheet is shown in Appendix 3. These data sheets are kept in a folder in the field vehicle under the custody of the Sr. Environmental Specialist returned to the ESS Building. After the sampling trip has been completed, samples are transported to the Fish Community Assessment Laboratory, located in the ESS building.

The sample information (sample number, waterbody, location, *etc*.) is recorded on the Log Sheet from NC DWR Stream Fish Community Assessment Program Samples (Appendix 1). This log sheet tracks all the samples that have been collected for a particular year. The Sr. Environmental Specialist assigns the Sample Number in numerical order. The first sample collected each year is Sample No. 1, the second sample is Sample No. 2, the third sample is Sample No. 3, etc. The sample numbers for 2005 took the form of 2005-01, 2005-02, 2005-03, *etc*. A sample number is assigned to a sample only after the sample has been collected. The log sheet and the field data sheets are stored in a 3-ring binder labeled "Field Data Sheets" in the Sr. Environmental Specialist's office at the ESS Building.

Physical habitat and water quality data that are collected include specific conductance, dissolved oxygen, temperature, pH, habitat description, average stream width and depth, water clarity (e.g., clear, slightly turbid, turbid, tannin stained, or blackwater, *etc*.), and substrate. These data are also recorded on the Stream Fish Community Assessment Program Field Data Sheet (Appendix 2).

SAMPLE COLLECTION

Essential sampling equipment that should accompany the Staff when sampling are listed in Table 8.

Table 8. Field sampling equipment.

County, state, and topographic maps	Chest waders and rubber gloves
Digital camera and charger	Measuring boards
Appropriate identification keys and field guides	Data sheets, pens, pencils, and waterproof markers
Assorted jars and plastic buckets with lids	Formalin and 95 percent ethanol
GPS unit	Measuring chain, thread, tape measure, and flagging tape
Dipnets (1/8 in. mesh) and assorted sizes of seines	Identification labels, tags, and rubber bands
Backpack electrofishing units	First aid kit, cardiac resuscitation unit, and insect repellent
Electrofishing batteries and chargers	Large fish preservation containers
Electrofishing probes and replacement rings	Water quality instruments

The number of personnel required to efficiently and effectively sample a 600 ft. wadeable section of stream is listed in Table 9. Typically, one-half of the sampling crew is outfitted with backpack electrofishing units and the other half with dip nets and buckets.

Table 9. Sampling personnel required to effectively sample streams of varying widths.

Stream width (m)	No. of electrofishers	No. of netters
≤ 3	1	1
3 to 10	2	2
10 to 15	2 or 3	2 or 3
> 15	3 or 4	3 or 4

Fish in the delineated stretch of stream are collected in a two-pass depletion technique using backpack electrofishing units and persons netting the stunned fish. Staff members collect samples by first moving in an upstream direction. After a short break, 5 to 10 minutes to allow the water to clear, sample collection is continued by staff members moving back downstream. All micro- and macrohabitats (riffles, pools, runs, snags, undercuts, deadfalls, quiescent leaf-covered substrates, *etc*.) should be thoroughly sampled. Electrofishing downstream into a seine should also be performed wherever there are significant riffles. Stunned fish are netted and placed into buckets with water that is frequently changed to minimize stress and mortality.

Details of the backpack electrofisher use and operation are given in the operator's manual and should be read carefully by all staff before using the equipment. Safety concerns require the wearing of chest waders and rubber gloves when the electrofishing unit is in operation.

After collection, all readily identifiable fish are examined for diseases, sores, lesions, fin damage, and skeletal anomalies, measured (total length to the nearest 1 mm), and then released. All data are recorded on the Stream Fish Community Assessment Program Field Data Sheet (Appendix 2). If a species is represented by multiple ages, a "Y" (for yes) is written in the margin of the data sheet across from the species name. If a species is not represented by multiple ages, a "N" (for no) is written. Deformed or diseased fish are also noted on the data sheet by circling the total length measurement of the affected fish. In addition, it is suggested that digital pictures be taken of any unusually deformed or diseased fish.

Once the first 50 specimens of a species are measured, the remaining fish of that particular species are just counted and released. All other fish (i.e., those fish that are not readily identifiable) are preserved in 10 percent formalin and returned to the laboratory for identification, examination, and total length measurement. If large (> 300 mm), unidentifiable fish are retained, the abdominal cavity should be injected with formalin soon after preservation or as soon as possible before the end of the sampling day.

SAMPLE IDENTIFICATION TAGS

Two sample identification tags (containing waterbody name, road crossing, county, date, and sample collection number) are completed and placed inside and attached outside every sample container (plastic

bucket or jar). Because formalin is the only preservative used, it is understood by staff that the samples are preserved in formalin and labeling of the sample container as to containing formalin is not necessary. Collectors' names are not listed on the labels because that information has been previously recorded on the Fish Community Assessment-IBI Data Sheet (Appendix 2). It is not necessary to record on the data sheet or the sample identification tag what analysis is to be done on the sample because samples are only preserved and returned to the laboratory if the species level identification is to be performed in the laboratory.

FIELD WATER QUALITY MEASUREMENTS

Measurements made in the field include water temperature, specific conductance, pH, stream flow (low, normal, high), water clarity (clear, slightly turbid, turbid, tannin stained, or blackwater), and dissolved oxygen. Field measurements are discrete and are made *in situ* by field staff at the time of the station visit. All field activities are to be performed in accordance with the Intensive Survey Branch's SOP (NCDENR 2011). In addition to the NC DWR's Intensive Survey Branch's SOP sections cited in Table 10, the instruction manual for the appropriate meter should also be consulted.

Table 10. Field measurement method references and reporting levels. Adopted from the Intensive Survey Branch's SOP (NCDENR 2011).

Parameter	Intensive Survey Branch's SOP & section[1]	EPA method	Reported to nearest
Water temperature	III.1	170.1	0.1 ºC
Dissolved oxygen	III.3	360.1	0.1 mg/L
pH	III.4	150.1	0.1 s. u.
Specific conductance	III.5	120.1	1 µS/cm

[1] Section numbers III.1 - III.5 refer to use of YSI combination meters.

All field meters are to be inspected and calibrated before each sampling trip and at minimum at the end of each day used. Field staff should record calibration information on the Field Meter Calibration Sheet (Appendix 4). This calibration form, which was adopted from the NC DWR's Intensive Survey Branch's SOP, is stored in a 3-ring binder labeled "Stream Fish Community Assessment Water Quality Meter Calibration Log" in the Stream Fish Community Assessment Program's Laboratory. Specific calibration procedures are documented in each meter's manufacturers' instruction manual. For pH, a two-point calibration (4.0 and 7.0 s.u.) is performed. Dissolved oxygen meters should be calibrated using the air calibration method. Specific conductance is calibrated against 1000 µS/cm and checked against 500 µS/cm standards.

Meters may be checked against standards periodically throughout the day and recalibrated if any of the following conditions occur:

- Physical shock to meter;
- Dissolved oxygen membrane is touched, fouled, punctured, or dries out;
- Unusual (high or low for the particular site) or erratic readings, or excessive drift;
- Extreme readings (e.g., extremely acidic or basic pH; dissolved oxygen saturation >120 percent); or
- Measurements are outside of the range for which the meter was calibrated.

HABITAT ASSESSMENT

A method has been developed by the Biological Assessment Branch to evaluate the physical habitats of a stream (Appendices 5 and 6). The narrative descriptions of eight (Mountain/Piedmont) or seven (Coastal Plain and Sand Hills) habitat characteristics, including channel modification, amount of instream habitat, type of bottom substrate, pool variety, riffle frequency, length and width, bank stability, light penetration, and riparian zone width, are converted into numerical scores. The total habitat score ranges between 1 and 100. Higher numbers suggest better habitat quality, but criteria have not been developed to assign impairment ratings.

SAMPLE HANDLING AND CUSTODY

Stunned fish are collected and temporarily stored in a bucket filled with stream water. Readily identifiable fish are counted and measured in the field and then released. If the sampling trip necessitates an

overnight stay, samples are stored in the cargo portion of the field vehicle, which is kept locked whenever staff members are away from the vehicle.

Samples are stored on bench space in the Fish Community Assessment Laboratory in the ESS Building until the fish have been properly preserved in formalin (usually 1-2 weeks or until the fish no longer are floating in the preservative). Once properly preserved, the sample can then be processed.

LABORATORY PROCESSING OF FISH SAMPLES

After the fish have been properly preserved in formalin (usually 1-2 weeks or until the fish no longer are floating in the preservative), the sample can be processed. The preservative is decanted under a hood (or other means providing appropriate ventilation) and discarded. The sample is rinsed with tap water several times and then allowed to soak in tap water for approximately one hour. The sample is sorted and each fish is identified to the **species** level and its total length measured to the nearest 1 millimeter. All laboratory-derived data are recorded on the Stream Fish Community Assessment Program Field Data Sheet (Appendix 3). Deformed or diseased fish are also noted on the data sheet by circling the total length measurement of the affected fish. If a species is represented by multiple ages, a "Y" (for yes) is written in the margin of the data sheet across from the species name. If a species is not represented by multiple ages, a "N" (for no) is written. Problematic identifications are verified by personnel from the North Carolina State Museum of Natural Science.

YOUNG-OF-YEAR CONSIDERATIONS AND ADJUSTMENTS

Young-of-year (YOY) fish may pose several challenges when applying the IBI metrics to a fish community sample (Angermeier and Karr (1986) and Angermeier and Schlosser (1987). Assessments made during the spring and early summer (April-June) tend to avoid these challenges. However, samples collected later in the summer and fall may contain an abundance of YOY fish. Individuals of a species who spawn in late summer or fall or from a late hatching cohort are not considered YOY when collected the following year (after January 1st) even though such individuals may be noticeably smaller than an earlier hatching cohort.

In some instances, depending upon the mildness of the winter and early spring, YOY fish (for example, redfin pickerel, creek chubsucker, bluegill, and redbreast sunfish), may already be present in samples collected during the spring. Assessments made in mid- to late June require careful attention and sometimes, professional judgment.

Efforts are made to not collect YOY fish, and, if collected, all YOY fish are excluded from all NCIBI calculations. Between July 1 and December 30, when most YOY may be collected, Table 4 should used as a guidance for the determination of YOY cut-off lengths. If a length for a particular species is not listed, best professional judgment or new knowledge of the life history of the species in North Carolina or the Southeast may be used for individuals collected where there may be doubt as to whether or not a fish is a YOY fish.

ACQUIRED DATA

All data are generated through the Stream Fish Community Assessment Program field activities and consequent laboratory analyses, with three exceptions:

- Geo-referenced (latitude and longitude) data are obtained from Maptech Terrain Navigator® software or from a Garmin GPS meter. These data are used in Geographic Information System mapping software and in describing the exact location from which a sample was collected.
- Watershed drainage areas for each site are obtained from the U. S. Geological Survey (http://water.usgs.gov/osw/streamstats/north_carolina.html) or from DWR's geographical information system software/data layers.
- Species lists for each basin are compiled from up-to-date taxonomic keys listed in the Literature Cited and Suggested References section, from data previously collected by the Stream Fish Community Assessment Program, and from other researchers at universities and state and federal resource agencies. These data aid in the accurate identification of fish species by listing which species are typically found or are not found in a particular river basin. Species lists are available at: http://portal.ncdenr.org/web/wq/ess/bau/nativefish.

COMPONENTS OF THE QA/QC PLAN

A detailed description of the Stream Fish Community Assessment Program Quality Assurance Project Plan can be found at http://portal.ncdenr.org/web/wq/ess/bau.

The Sr. Environmental Specialist will be responsible for overseeing the collection of all stream fish community assessment program samples. Personnel from the Biological Assessment Branch will provide primary sampling assistance. Other experienced field biologists within the Environmental Sciences Section or other agencies may be used as needed.

Prior to sampling, a fish species list will be compiled of all the species known or suspected to occur within the basin or stream under study. Such a list is compiled from species distribution maps (Menhinick 1991 and amended with Biological Assessment Branch data and data from other regional fisheries researchers). The list will also show which species may be afforded protection at the federal or state level and which would require field identification and immediate release.

As discussed in the Sample Collection section, as many readily and easily identifiable fish are processed stream-side as possible. A fish whose specific identity is unknown, questionable, or disputed between the fisheries biologists is properly preserved for later laboratory identification.

Examples of a species or a specimen(s) that should be preserved are ones that:

- can not be readily and easily identified in the field;
- are not represented in the Reference Collection (a list of species in the Reference Collection is kept with the Reference Collection in the Fish Laboratory and should be consulted prior to sampling) ;
- are of known taxonomic value (e.g., a poorly understood or undescribed species (such as the Carolina redhorse) or rarely collected size classes of a species);
- represent a new distributional record; or
- may be a hybrid.

Additional suggested guidelines for when to preserve specimens may be found in Walsh and Meador (1998).

Random samples, identified in the laboratory, are re-processed for accurate and correct determinations of identity and presence or absence of multiple age classes. Because of the relatively limited icthyofauna within any specific river basin, the likelihood of misidentifications is not as great as is the case for other taxonomic groups (e.g., benthic invertebrates or phytoplankton). Consequently, at least 10% of the samples from each river basin are selected for re-identification using a electronic random number generator or electronic dice (http://www.random.org/ or http://www.roll-dice-online.com/). The sample number (sorted in numerical order) corresponding with the random number or die number is re-identified. Any misidentifications or inaccuracies in multiple age class determinations are resolved. The data sheet

from which the sample was chosen for verification is signed and dated attesting to the accuracy and completeness of the sample.

A Reference Collection shall be maintained. Except for federally- and state-recognized rare, endangered, or threatened species (Table 11), the Reference Collection should include at least one specimen of every freshwater species found in the state. Species afforded the extra state or federal protection and which were collected accidentally (Incidental Take) shall be deposited in the North Carolina State Museum of Natural Sciences (NCSMNS). The Reference Collection shall be maintained and utilized for laboratory identifications of problematic species. Comparisons of such specimens or species may also be made to specimens in the NCSMNS. A list of species in the Reference Collection is kept with the Reference Collection in the Stream Fish Community Assessment Program's Fish Laboratory and should updated as needed.

Table 11. Phylogenetic listing of the state and federally protected endangered and threatened species (from LeGrand, *et al*. 2012).

Species	Common Name	State Status	Federal Status
Lampetra aepyptera	Least Brook Lamprey	Threatened	
L. appendix	American Brook Lamprey	Threatened	
Acipenser brevirostrum	Shortnose Sturgeon	Endangered	Endangered
Polyodon spathula	Paddlefish	Endangered	
Erimonax monachus	Spotfin Chub	Threatened	Threatened
Hybopsis rubifrons	Rosyface Chub	Threatened	
Notropis bifrenatus	Bridle Shiner	Endangered	
Notropis mekistocholas	Cape Fear Shiner	Endangered	Endangered
Moxostoma robustum	Robust Redhorse	Endangered	
M. sp. cf. *macrolepidotum*	Sickelfin Redhorse	Threatened	
M. sp. cf. erythrurum	Carolina Redhorse	Threatened	
Scartomyzon ariommus	Bigeye Jumprock	Threatened	
Thoburnia hamiltoni	Rustyside Sucker	Endangered	
Noturus flavus	Stonecat	Endangered	
N. furiosus	Carolina Madtom	Threatened	
N. gilberti	Orangefin Madtom	Endangered	
Menidia extensa	Waccamaw Silverside	Threatened	
Cottus carolinae	Banded Sculpin	Threatened	
Etheostoma acuticeps	Sharphead Darter	Threatened	
E. inscriptum	Turquoise Darter	Threatened	
E. perlongum	Waccamaw Darter	Threatened	
Percina burtoni	Blotchside Logperch	Endangered	
P. caprodes	Logperch	Threatened	
P. rex	Roanoke Logperch	Endangered	Endangered
Elassoma boehlkei	Carolina Pygmy Sunfish	Threatened	

All specimens returned to the laboratory for identification which do not become part of the Reference Collection or of the Teaching Collection (a collection maintained to educate school groups, tours, or citizens at public fair and forums) will be donated to the NCSMNS. The State Ichthyologist (and staff) will serve as the qualified, independent fish taxonomic specialist(s). All specimens are verified for correctness of species identification prior to being incorporated into the NCSMNS Collection. Any misidentifications or other discrepancies will be communicated back by the NCSMNS staff.

DATA MANAGEMENT

Field- and laboratory-generated data from a single sampling event are recorded on the same Stream Fish Community Assessment Program Field Data Sheet (Appendices 2 and 3). A vertical bar "**I**" is used to separate and distinguish field data (specimens identified, measured, and released in the field) from lab data (specimens identified and measured in the lab). This distinction is made so that staff members know

and can keep track of which specimens were processed in the field and which specimens were returned to the laboratory.

Data are keyed by the Sr. Environmental Specialist into the Stream Fish Community Assessment Program's Microsoft Access® 2010 database. Annually, this results in almost 1,500 records (~20 species per site X 75 sites sampled annually = 1,500 species records). The biologists review the data for completeness, data entry errors, unlikely or impossible values, *etc*. Copies of this database reside on the Sr. Environmental Specialist's drive on the ESS server and on BAB's drive on the ESS server. Tape backups are run daily on the ESS servers. The database is updated on a as needed basis whenever samples are completed or whenever errors in previously entered data are identified.

All calculations that result in any data summaries as shown in the North Carolina Fish Community Reports (Appendix 8) are generated by programs in the Stream Fish Community Assessment Program's Microsoft Access® 2010 database.

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NC DIVISION OF WATER RESOURCES

STREAM FISH COMMUNITY ASSESSMENT PROGRAM SAMPLES LOG SHEET

YEAR _____

Sample No.	Waterbody	Location	County	Collection Date	Basin	Study

NC DIVISION OF WATER RESOURCES

STREAM FISH COMMUNITY ASSESSMENT PROGRAM FIELD DATA SHEET

UNIQUE SITE IDENTIFIER	SAMPLE NO.
STREAM	SAMPLE DATE
LOCATION	TIME
COUNTY	NO. OF SHOCKING UNITS
RIVER BASIN	DURATION (sec.)
8 Digit HUC	SAMPLING PERSONNEL
LATITUDE	LOCATION OF REACH
LONGITUDE	SEINE USED ? (Y/N)
DRAINAGE AREA (mi.^{2})	SAMPLE IDENTIFIED BY
STREAM INDEX NO.	DATE SAMPLE IDENTIFIED
STREAM CLASSIFICATION	DATA ENTERED BY
HABITAT SCORE	DATE OF DATA ENTRY
ELEVATION (ft.)	

SPECIFIC CONDUCTANCE (µS/cm)	AVG. STREAM WIDTH (m)
DISSOLVED OXYGEN (mg/L)	AVG. STREAM DEPTH (m)
TEMPERATURE (ºC)	WATER CLARITY (clear, turbid, blackwater)
pH	SUBSTRATE TYPE(s)
HABITAT DESCRIPTION	

Species	Total No.	Length	Length	Length	Length	Length	Length	Length	Length	Length

PAGE ___ OF ___

NC DIVISION OF WATER RESOURCES

STREAM FISH COMMUNITY ASSESSMENT PROGRAM FIELD DATA SHEET

STREAM	SAMPLE NO.
SAMPLE LOCATION	SAMPLE DATE

Species	Total No.	Length	Length	Length	Length	Length	Length	Length	Length	Length

SFCAP SOP Appendix 3. Example of a completed Stream Fish Community Assessment Program Field Data Sheet. ***Note: this data sheet was the version used between 2006 and 2013.***

PAGE 1 OF 2

NC DIVISION OF WATER QUALITY

STREAM FISH COMMUNITY ASSESSMENT PROGRAM FIELD DATA SHEET

UNIQUE SITE IDENTIFIER	AF30	SAMPLE NO.	2010-34
STREAM	Britten Creek	SAMPLE DATE	08 June 2010
LOCATION	NC 9	TIME	1030 - 1132
COUNTY	Polk	NO. OF SHOCKING UNITS	2
RIVER BASIN	BRD	DURATION (sec.)	2388 + 2596 = 4984
SUBBASIN	02	SAMPLING PERSONNEL	DeRowanduis, Swanson, Tracy, Lyder, Bow
LATITUDE	35.34167	LOCATION OF REACH	600' up, beginning @ culvert
LONGITUDE	-82.18194	SEINE USED ? (Y/N)	Y - used green nets
DRAINAGE AREA (mi.²)	6.8	SAMPLE IDENTIFIED BY	BHTracy
STREAM INDEX NO.	9-24-43	DATE SAMPLE IDENTIFIED	25 August 2010
STREAM CLASSIFICATION	C	DATA ENTERED BY	BHTracy
HABITAT SCORE	96	DATE OF DATA ENTRY	10 Sept. 2010
ELEVATION (ft)	840'	Next time use the seine if sufficient current	

ELEVATION (ft) at concrete anchor

Low gradient @ culvert (1st 100') then changing to high gradient w/ plunges

SPECIFIC CONDUCTANCE (µmhos/cm)	37	AVG. STREAM WIDTH (m)	9
DISSOLVED OXYGEN (mg/L)	8.5	AVG. STREAM DEPTH (m)	0.4
TEMPERATURE (°C)	19.4	WATER CLARITY (clear, turbid, blackwater)	cloudy silted
pH	6.1	SUBSTRATE TYPE(s)	cobble, boulder, bedrock

HABITAT DESCRIPTION plunge pools; chutes + riffles; soft pool @ bridge

No Effort below ?

	Species	Total No.	Length	Length	Length	Length	Length	Length	Length	Length	Length	Length
Y	Bluehead Chub	64	142	93	170	67	45	54	65	77	72	65
	" (+8)		86	60	65	72	60	43	64	52	156	126
	" (+6)		52	152	70	70	45	65	58	92	67	95
	"		64	90	62	109	77	67	106	67	93	76
	"		86	73	75	70	85	74	66	92	110	53
Y	Fieryblack Shiner	86	63	54	64	96	82	64	79	48	55	63
	" (+6)		82	78	60	78	62	73	78	71	77	65
	" (+29)		100	87	45	65	80	52	47	90	57	46
	" (+1)		77	62	85	60	78	70	71	61	73	42
	"		62	67	67	90	38	37	63	70	37	71
Y	Redbreast SF	33	126	105	150	122	86	165	92	88	110	85
	"		74	93	94	70	68	63	76	71	96	100
	"		75	96	55	116	61	55	78	62	45	96
Y	M. Mad tom	33	126	88	110	81	106	93	68	90	72	104
	"		86	96	68	106	98	73	92	105	73	95
	"		88	75	94	86	88	92	102	73	72	79
poss N	Sandbar Shiner	3	78	82	77							
Y	Spotfail Shiner	59	85	75	91	103	85	73	95	89	96	82
	" (+8)		90	88	85	74	92	76	88	84	83	82
	" (+1)		76	75	95	72	87	95	83	85	82	87
poss Y	Stripeback Jumprock	22	110	162	95	105	110	129	86	700	92	110
	"		145	140	152	186	157	155	172	120	140	162
	"		102	109								
Y	Flat Bullhead	17	135	163	166	110	110	93	66	109	112	150
	"		116	110	162	80	108	66	135			
Y	Greenfin Shiner	5	71	75	56	68	52					
Y	Northern Hog Sucker	3	250	186	120							
N	Snail Bullhead	1	152									
Y	Piedmont Shiner	13	44	50	44	42	45	44	50	63	42	48
	"		47	41	43							

Version 3
February 23, 2006

95% @ 404 – N. hudsonius - 5
– C. pleurobevbs - 4
– C. chloristia - 1

OVER →

PAGE 2 OF 2

NC DIVISION OF WATER QUALITY

STREAM FISH COMMUNITY ASSESSMENT PROGRAM FIELD DATA SHEET

STREAM	Britten Creek	SAMPLE NO.	# 2010-54
SAMPLE LOCATION	NC 9	SAMPLE DATE	08 June 2010

	Species	Total No.	Length	Length	Length	Length	Length	Length	Length	Length	Length	Length
YOY -	LMB	—	50	45	42	43	48	42				
N -	Bluegill	1	44									
Y -	Sengreen Darter	39	43	70	52	48	45	47	52	47	44	55
	"		52	46	52	57	57	44	52	42	46	52
	"		55	62	61	45	41	53	51	45	45	53
N -	Warmouth	1	65									
N -	Piedmont Darter	2	56	52								
↑	Spottail Shiner	—	82	70	85	86	83	81	93	80	101	71
	"		77	71	69	83	83	78	94	91	90	88
N -	V-Lip Redhorse	1	236									
popeye Y -	Rosyside Dace	3	39	59	66							
N -	Tess Darter	5	46	42	45	45	43					
N -	Santee Chub	2	43	38								
↑	Sengreen Darter	—	45	46	63	50	62	43	54	51	44	
↑	RBSF	—	62	67	80							
↑	M. Madtom	—	100	97	94							
N -	Cyprinella nivea	1	71									
	12/21sp =	57%										

Version 3
February 23, 2006

SFCAP SOP Appendix 4. Field meter calibration sheet.

Water Quality Monitoring Field Meter Calibration Sheet

Collector(s):

Study:

Sampling Location:

Meter Model:

Meter / Sonde Serial No:

	Date yy/mm/dd	Time 24hr hh:mm	Initials
Pre-Sampling Calibration			
Post-Sampling Check			

Miscellaneous (Does not apply to YSI or Accumet Meters)

	Battery Level (V)		Stirrer Working?
Pre-Sampling Calibration			Y / N
Post-Sampling Check			Y / N

Battery Ranges = Surveyor: internal- 7.2-7.5V, external- 11-13V; Quanta: 4.0-4.5V

Barometer Calibration (mmHg)
**YSI Pro Plus Meters Only*

Initial Reading	Calibrated Value

Dissolved Oxygen (mg/L)

	Temp. °C	Initial % Saturation	Barometric Pressure (mmHg)	Altitude (ft.)	D.O. Table Value	Initial Meter Reading (mg/L)	Calibrated Meter Reading (mg/L)	Calibrated % Saturation
Pre-Sampling Calibration								
Post-Sampling Check								
					Within ± 0.5 ? Y / N			

Specific Conductance (µS/cm at 25ºC)

	Dry Air [1, 2] Zero (0)		Conductivity Standard [3] Lot #: Value:		Calibration Check Lot #: Value:
	Initial Meter Reading	Calibrated [4] Meter Reading	Initial Meter Reading	Calibrated [4] Meter Reading	Initial Meter Reading
Pre-Sampling Calibration					
Post-Sampling Check	Within ± 2? Y / N		Within ±10%? Y / N		Within ±10% Y / N

±10% Ranges for Sp. Cond.

Standard	Range
100	90 to 110
500	450 to 550
1,000	900 to 1,100
10,000	9,000 to 11,000
15,000	13,500 to 16,500
50,000	45,000 to 55,000

NOTE: Quanta reads in mS/cm; move decimal 3 places right for µS/cm.

[1] Dry Air CALIBRATIONS are conducted for 4a and MS5 Hydrolabs only.

[2] Dry Air CHECKS (confirmation of zero in dry air) are conducted for YSI 85, YSI 6920, YSI Pro Plus & Quanta meters.

[3] Conductivity standards are used to CHECK the YSI 85 meter and to CALIBRATE all Hydrolab meters and the YSI 6920 & YSI Pro Plus.

[4] Does not apply to Dry Air CHECKS or Conductivity Standard CHECKS (leave blank).

pH (SU)

	Buffer #1 7.0 Lot #: Buffer Temp:		Buffer #2 4.0 / 10.0 Lot #: Buffer Temp:		Slope Efficiency[5]	Confirmation Buffer 7.0
	Initial Meter Reading	Calibrated Meter Reading	Initial Meter Reading	Calibrated Meter Reading		Meter Reading
Pre-Sampling Calibration						
Post-Sampling Check	Within ± 0.2? Y / N		Within ± 0.2? Y / N			Within ± 0.1? Y / N

[5] Slope efficiency applies to Accumet meters only (does not apply to Hydrolab or YSI meters).

Comments:

Keep original on file for 5 years

Ver. 06/05/2012

11/13 Revision 8

Habitat Assessment Field Data Sheet
Mountain/ Piedmont Streams

Biological Assessment Branch, DWR **TOTAL SCORE**

Directions for use: The observer is to survey a **minimum of 100 meters with 200 meters preferred** of stream, preferably in an **upstream** direction starting above the bridge pool and the road right-of-way. The segment which is assessed should represent average stream conditions. To perform a proper habitat evaluation the observer needs to get into the stream. To complete the form, select the description which best fits the observed habitats and then circle the score. If the observed habitat falls in between two descriptions, select an intermediate score. A final habitat score is determined by adding the results from the different metrics.

Stream_____Location/road: _____(Road Name_____)County_____

Date_____**CC#**_____Basin_____Subbasin_____

Observer(s)_____ Type of Study: ☐ Fish ☐Benthos ☐ Basinwide ☐Special Study (Describe) _____

Latitude _____Longitude _____Ecoregion: ☐ MT ☐ P ☐ Slate Belt ☐ Triassic Basin

Water Quality: Temperature_____^{0}C DO _____mg/l Conductivity (corr.) _____µS/cm pH _____

Physical Characterization: Visible land use refers to immediate area that you can see from sampling location - include what you estimate driving thru the watershed in watershed land use.

Visible Land Use: _____%Forest _____%Residential _____%Active Pasture _____% Active Crops
_____%Fallow Fields _____% Commercial _____%Industrial _____%Other - Describe:_____

Watershed land use : ☐Forest ☐Agriculture ☐Urban ☐ Animal operations upstream

Width: (meters) Stream_____ Channel (at top of bank)_____ **Stream Depth:** (m) Avg_____Max ____
☐ Width variable ☐ Large river >25m wide
Bank Height (from deepest part of riffle to top of bank-first flat surface you stand on): (m)_____

Bank Angle: _____° or ☐ NA (Vertical is 90°, horizontal is 0°. Angles > 90° indicate slope is towards mid-channel, < 90° indicate slope is away from channel. NA if bank is too low for bank angle to matter.)
☐ Channelized Ditch
☐Deeply incised-steep, straight banks ☐Both banks undercut at bend ☐Channel filled in with sediment
☐ Recent overbank deposits ☐Bar development ☐Buried structures ☐Exposed bedrock
☐ Excessive periphyton growth ☐ Heavy filamentous algae growth ☐Green tinge ☐ Sewage smell
Manmade Stabilization: ☐N ☐Y: ☐Rip-rap, cement, gabions ☐ Sediment/grade-control structure ☐Berm/levee
Flow conditions : ☐High ☐Normal ☐Low
Turbidity: ☐Clear ☐ Slightly Turbid ☐Turbid ☐Tannic ☐Milky ☐Colored (from dyes)
Good potential for Wetlands Restoration Project?? ☐ **YES** ☐**NO Details**_____

_____

Channel Flow Status

Useful especially under abnormal or low flow conditions.

A. Water reaches base of both lower banks, minimal channel substrate exposed ..... ☐
B. Water fills >75% of available channel, or <25% of channel substrate is exposed..... ☐
C. Water fills 25-75% of available channel, many logs/snags exposed..... ☐
D. Root mats out of water..... ☐
E. Very little water in channel, mostly present as standing pools..... ☐

Weather Conditions:_____**Photos:** ☐N ☐Y ☐ Digital ☐35mm

Remarks:_____

_____

_____

_____

I. Channel Modification

	Score
A. channel natural, frequent bends	5
B. channel natural, infrequent bends (channelization could be old)	4
C. some channelization present	3
D. more extensive channelization, >40% of stream disrupted	2
E. no bends, completely channelized or rip rapped or gabioned, etc.	0

☐ Evidence of dredging ☐Evidence of desnagging=no large woody debris in stream ☐Banks of uniform shape/height

Remarks_____ Subtotal____

II. Instream Habitat: Consider the percentage of the reach that is favorable for benthos colonization or fish cover. If >70% of the reach is rocks, 1 type is present, circle the score of 17. Definition: leafpacks consist of older leaves that are packed together and have begun to decay (not piles of leaves in pool areas). Mark as Rare, Common, or Abundant.

____**Rocks** ____**Macrophytes** ____**Sticks and leafpacks** ____**Snags and logs** ____**Undercut banks or root mats**

AMOUNT OF REACH FAVORABLE FOR COLONIZATION OR COVER

	>70% Score	40-70% Score	20-40% Score	<20% Score
4 or 5 types present	20	16	12	8
3 types present	19	15	11	7
2 types present	18	14	10	6
1 type present	17	13	9	5
No types present	0			

☐ No woody vegetation in riparian zone Remarks_____ Subtotal_____

III. Bottom Substrate (silt, sand, detritus, gravel, cobble, boulder) Look at entire reach for substrate scoring, but only look at riffle for embeddedness, and use rocks from all parts of riffle-look for "mud line" or difficulty extracting rocks.

	Score
A. substrate with good mix of gravel, cobble and boulders	
1. embeddedness <20% (very little sand, usually only behind large boulders)	15
2. embeddedness 20-40%	12
3. embeddedness 40-80%	8
4. embeddedness >80%	3
B. substrate gravel and cobble	
1. embeddedness <20%	14
2. embeddedness 20-40%	11
3. embeddedness 40-80%	6
4. embeddedness >80%	2
C. substrate mostly gravel	
1. embeddedness <50%	8
2. embeddedness >50%	4
D. substrate homogeneous	
1. substrate nearly all bedrock	3
2. substrate nearly all sand	3
3. substrate nearly all detritus	2
4. substrate nearly all silt/ clay	1

Remarks_____ Subtotal_____

IV. Pool Variety Pools are areas of deeper than average maximum depths with little or no surface turbulence. Water velocities associated with pools are always slow. Pools may take the form of "pocket water", small pools behind boulders or obstructions, in large high gradient streams, or side eddies.

	Score
A. Pools present	
1. Pools Frequent (>30% of 200m area surveyed)	
a. variety of pool sizes	10
b. pools about the same size (indicates pools filling in)	8
2. Pools Infrequent (<30% of the 200m area surveyed)	
a. variety of pool sizes	6
b. pools about the same size	4
B. Pools absent	0

Subtotal_____

☐ Pool bottom boulder-cobble=hard ☐ Bottom sandy-sink as you walk ☐ Silt bottom ☐ Some pools over wader depth

Remarks_____

Page Total_____

V. Riffle Habitats

Definition: Riffle is area of reaeration-can be debris dam, or narrow channel area.

	Riffles **Frequent** Score	Riffles **Infrequent** Score
A. well defined riffle and run, riffle as wide as stream and extends 2X width of stream....	16	12
B. riffle as wide as stream but riffle length is not 2X stream width	14	7
C. riffle not as wide as stream and riffle length is not 2X stream width	10	3
D. riffles absent.....	0	

Channel Slope: ☐Typical for area ☐Steep=fast flow ☐Low=like a coastal stream Subtotal_____

VI. Bank Stability and Vegetation

A. Erosion

1. No, or very little, erosion present 7
2. Erosion mostly at outside of meanders..... 6
3. Less than 50% of banks eroding..... 3
4. Massive erosion..... 0 Erosion Score_____

B. Bank Vegetation

1. Mostly mature trees (>12" DBH) present 7
2. Mostly small trees (<12" DBH) present, large trees rare 5
3. No trees on bank, can have some shrubs and grasses..... 3
4. Mostly grasses or mosses on bank 2
5. Little or no bank vegetation, bare soil everywhere ..... 0 Vegetation Score_____

Remarks_____ Subtotal_____

VII. Light Penetration Canopy is defined as tree or vegetative cover directly above the stream's surface. Canopy would block out sunlight when the sun is directly overhead. Note shading from mountains, but not use to score this metric.

	Score
A. Stream with **good** canopy with some breaks for light penetration	10
B. Stream with **full canopy** - breaks for light penetration absent.....	8
C. Stream with **partial** canopy - sunlight and shading are essentially equal.....	7
D. Stream with **minimal** canopy - full sun in all but a few areas.....	2
E. **No canopy** and no shading.....	0

Remarks_____ Subtotal_____

VIII. Riparian Vegetative Zone Width

Definition: Riparian zone for this form is area of natural vegetation adjacent to stream (can go beyond floodplain). Definition: A break in the riparian zone is any place on the stream banks which allows sediment or pollutants to directly enter the stream, such as paths down to stream, storm drains, uprooted trees, otter slides, etc.

FACE UPSTREAM

Dominant vegetation: ☐ Trees ☐ Shrubs ☐ Grasses ☐ Weeds/old field ☐Exotics (kudzu, etc)

	Lft. Bank Score	Rt. Bank Score
A. Riparian zone **intact** (no breaks)		
1. width > 18 meters.....	5	5
2. width 12-18 meters.....	4	4
3. width 6-12 meters.....	3	3
4. width < 6 meters.....	2	2
B. Riparian zone **not intact** (breaks)		
1. breaks rare		
a. width > 18 meters.....	4	4
b. width 12-18 meters.....	3	3
c. width 6-12 meters.....	2	2
d. width < 6 meters.....	1	1
2. breaks common		
a. width > 18 meters.....	3	3
b. width 12-18 meters.....	2	2
c. width 6-12 meters.....	1	1
d. width < 6 meters.....	0	0

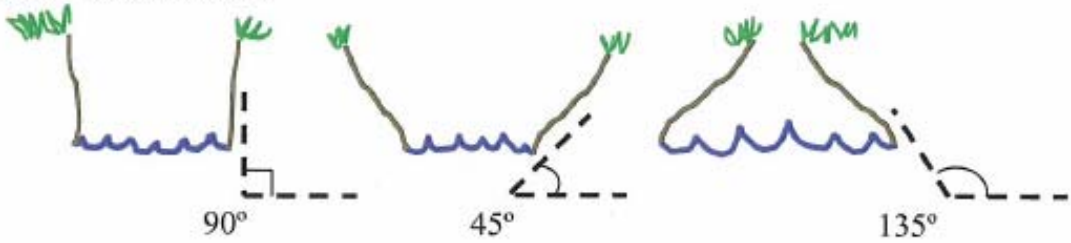
Remarks_____ Subtotal_____

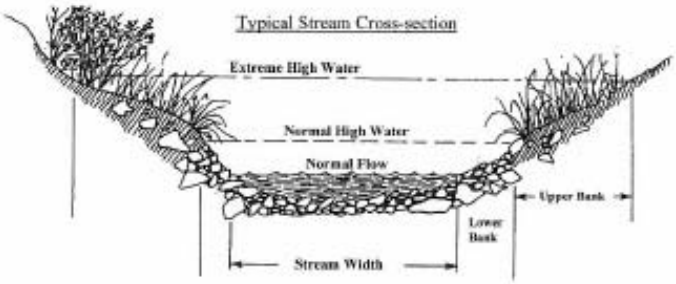
Page Total_____

☐ Disclaimer-form filled out, but score doesn't match subjective opinion-atypical stream. **TOTAL SCORE**_____

Supplement for Habitat Assessment Field Data Sheet

Diagram to determine bank angle:





This side is 45° bank angle.

Site Sketch:

Other comments:_____

11/13 Revision 9

Habitat Assessment Field Data Sheet
Coastal Plain Streams

TOTAL SCORE_____

Biological Assessment Branch, DWR
Directions for use: The observer is to survey a **minimum of 100 meters with 200 meters preferred** of stream, preferably in an **upstream** direction starting above the bridge pool and the road right-of-way. The segment which is assessed should represent average stream conditions. To perform a proper habitat evaluation the observer needs to get into the stream. To complete the form, select the description which best fits the observed habitats and then circle the score. If the observed habitat falls in between two descriptions, select an intermediate score. A final habitat score is determined by adding the results from the different metrics.

Stream_____Location/road: _____(Road Name_____)County_____

Date_____**CC#**_____Basin_____Subbasin_____

Observer(s)_____ Type of Study: ☐ Fish ☐Benthos ☐ Basinwide ☐Special Study (Describe) _____

Latitude _____Longitude _____Ecoregion: ☐ CA ☐ SWP ☐ Sandhills ☐ CB

Water Quality: Temperature_____^{0}C DO _____mg/l Conductivity (corr.) _____µS/cm pH _____

Physical Characterization: Visible land use refers to immediate area that you can see from sampling location. Check off what you observe driving thru the watershed in watershed land use.

Visible Land Use: _____%Forest _____%Residential _____%Active Pasture _____% Active Crops
_____%Fallow Fields _____% Commercial _____%Industrial _____%Other - Describe:_____

Watershed land use ☐ Forest ☐ Agriculture ☐Urban ☐ Animal operations upstream

Width: (meters) Stream_____ Channel (at top of bank)_____ **Stream Depth**: (m) Avg_____Max ____
☐ **Width variable** ☐**Braided channel** ☐**Large river >25m wide**
Bank Height (from deepest part of channel to top of bank): (m)_____

Flow conditions : ☐High ☐Normal ☐Low
Channel Flow Status
Useful especially under abnormal or low flow conditions.
A. Water reaches base of both banks, minimal channel substrate exposed ..... ☐
B. Water fills >75% of available channel, or <25% of channel substrate is exposed..... ☐
C. Water fills 25-75% of available channel, many logs/snags exposed..... ☐
D. Root mats out of water..... ☐
E. Very little water in channel, mostly present as standing pools..... ☐

Turbidity: ☐Clear ☐ Slightly Turbid ☐Turbid ☐Tannic ☐Milky ☐Colored (from dyes) ☐Green tinge
Good potential for Wetlands Restoration Project?? ☐ **YES** ☐ **NO Details**_____
_____

☐Channelized ditch
☐Deeply incised-steep, straight banks ☐Both banks undercut at bend ☐Channel filled in with sediment
☐Recent overbank deposits ☐Bar development ☐Sewage smell
☐Excessive periphyton growth ☐Heavy filamentous algae growth

Manmade Stabilization: ☐N ☐Y: ☐Rip-rap, cement, gabions ☐ Sediment/grade-control structure ☐Berm/levee
Weather Conditions:_____**Photos:** ☐N ☐Y ☐Digital ☐35mm

Remarks:_____
_____
_____

TYPICAL STREAM CROSS SECTION DIAGRAM ON BACK

I. Channel Modification

	Score
A. Natural channel-minimal dredging	15
B. Some channelization near bridge, or historic (>20 year old), and/or bends beginning to reappear..	10
C. Extensive channelization, straight as far as can see, channelized ditch	5
D. Banks shored with hard structure, >80% of reach disrupted, instream habitat gone	0

Remarks_____ Subtotal____

II. Instream Habitat: Consider the percentage of the reach that is favorable for benthos colonization or fish cover. If >50% of the reach is snags, and 1 type is present, circle the score of 16. Definition: leafpacks consist of older leaves that are packed together and have begun to decay (not piles of leaves in pool areas). Mark as Rare, Common, or Abundant.

____**Sticks** ____**Snags/logs** ____**Undercut banks or root mats** ____**Macrophytes** ____**Leafpacks**

AMOUNT OF REACH FAVORABLE FOR COLONIZATION OR COVER

	>50% Score	30-50% Score	10-30% Score	<10% Score
4 or 5 types present	20	15	10	5
3 types present	18	13	8	4
2 types present	17	12	7	3
1 type present	16	11	6	2

No substrate for benthos colonization and no fish cover.....0

☐ No woody vegetation in riparian zone Remarks_____ Subtotal_____

III. Bottom Substrate (silt, clay, sand, detritus, gravel) look at entire reach for substrate scoring.

	Score
A. Substrate types mixed	
1. gravel dominant	15
2. sand dominant	13
3. detritus dominant	7
4. silt/clay/muck dominant	4
B. Substrate homogeneous	
1. nearly all gravel	12
2. nearly all sand	7
3. nearly all detritus	4
4. nearly all silt/clay/muck	1

Remarks_____ Subtotal_____

IV. Pool Variety Pools are areas of deeper than average maximum depths with little or no surface turbulence. Water velocities associated with pools are always slow.

	Score
A. Pools present	
1. Pools Frequent (>30% of 100m length surveyed)	
a. variety of pool sizes	10
b. pools about the same size (indicates pools filling in)	8
2. Pools Infrequent (<30% of the 100m length surveyed)	
a. variety of pool sizes	6
b. pools about the same size	4
B. Pools absent	
1. Deep water/run habitat present	4
2. Deep water/run habitat absent	0
	Subtotal_____

Remarks_____ Page Total_____

V. Bank Stability and Vegetation

A. Erosion

1. No, or very little, erosion present 10
2. Erosion mostly at outside of meanders 6
3. Less than 50% of banks eroding 3
4. Massive erosion ..... 0 Erosion Score_____

B. Bank Vegetation

1. Mostly mature trees (>12" DBH) present 10
2. Mostly small trees (<12" DBH) present, large trees rare 7
3. No trees on bank, can have some shrubs and grasses 4
4. Mostly grasses or mosses on bank 3
5. Little or no bank vegetation, bare soil everywhere ..... 0 Vegetation Score_____

Remarks_____ Subtotal_____

VI. Light Penetration (Canopy is defined as tree or vegetative cover directly above the stream's surface. Canopy would block out sunlight when the sun is directly overhead).

	Score
A. Stream with **good** canopy with some breaks for light penetration	10
B. Stream with **full canopy** - breaks for light penetration absent.....	8
C. Stream with **partial** canopy - sunlight and shading are essentially equal.....	7
D. Stream with **minimal** canopy - full sun in all but a few areas.....	2
E. **No canopy** and no shading.....	0

Subtotal_____

Remarks_____

VII. Riparian Vegetative Zone Width

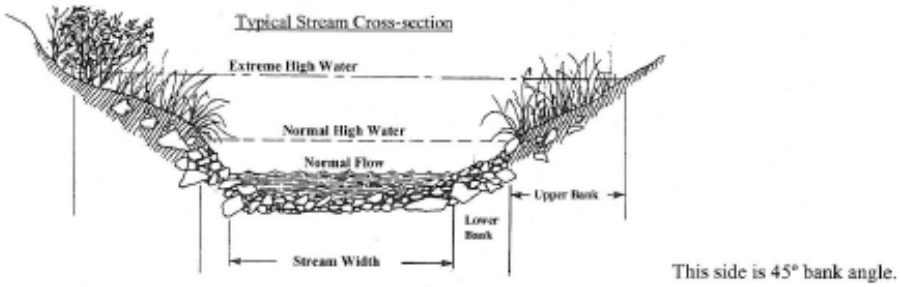
Definition: A break in the riparian zone is any area which allows sediment to enter the stream. Breaks refer to the near-stream portion of the riparian zone (banks); places where pollutants can directly enter the stream.

	Lft. Bank Score	Rt. Bank Score
A. Riparian zone **intact** (no breaks)		
1. zone width > 18 meters.....	5	5
2. zone width 12-18 meters.....	4	4
3. zone width 6-12 meters.....	3	3
4. zone width < 6 meters.....	2	2
B. Riparian zone **not intact** (breaks)		
1. breaks rare		
a. zone width > 18 meters.....	4	4
b. zone width 12-18 meters.....	3	3
c. zone width 6-12 meters.....	2	2
d. zone width < 6 meters.....	1	1
2. breaks common		
a. zone width > 18 meters.....	3	3
b. zone width 12-18 meters.....	2	2
c. zone width 6-12 meters.....	1	1
d. zone width < 6 meters.....	0	0

Remarks_____ Subtotal_____

Page Total_____

TOTAL SCORE _____


Typical Stream Cross-section
Extreme High Water
Normal High Water
Normal Flow
Upper Bank
Lower Bank
Stream Width
This side is 45° bank angle.

SFCAP SOP Appendix 7. Stream Fish Community Assessment Program Data Entry Log Sheet.

NC DIVISION OF WATER RESOURCES

STREAM FISH COMMUNITY ASSESSMENT PROGRAM DATA ENTRY LOG SHEET

YEAR ____

Sample No.	Waterbody	Date Identified	Date Data Entered	Date Data Checked	Date Data "Clean"

11/19/2013 2:59:55 PM

North Carolina Fish Community Report

Waterbody	Britten Cr	**No. Secs.**	4984		
Station	NC 9	**No. Units**	2		
County	Polk	**CPUE**	7.9		
Latitude	35.34167	**Width**	9	m	
Longitude	-82.18194	**Depth:**	0.4	m	
Ecoregion	P	**Drainage**	6.8	mi2	
8 Digit HUC	03050105	**Elevation**	840	ft	
8 HUC Name	Upper Broad River				
Basin	BRD				
Stream Index No.	9-29-43				
Stream Classification	C				
Level IV Ecoregion	Southern Inner Piedmont				

- [x] Reference Site
- [x] Basin Site
- [ ] Special Study

Collection No.	2010-34
Data Entry	BT
Date	6/8/2010
Station ID	AF30

Temperature	19.4	°C
Specific Conductance	37	µS/cm
Dissolved Oxygen	8.5	mg/L
pH	6.1	s.u.
Clarity	Clear	
Total Habitat Score	96	

NCIBI Score 54 **NCIBI Rating** Excellent

Family	Scientific Name	Trophic Status	Tolerance	Multiple Ages	No.	Exotics (True)
Catostomidae	Hypentelium nigricans	Insectivore	Intermediate	Yes	3	☐
Catostomidae	Moxostoma pappillosum	Insectivore	Intermediate	No	1	☐
Catostomidae	Scartomyzon rupiscartes	Insectivore	Intermediate	Yes	22	☐
Centrarchidae	Lepomis auritus	Insectivore	Tolerant	Yes	33	☐
Centrarchidae	Lepomis gulosus	Insectivore	Intermediate	No	1	☐
Centrarchidae	Lepomis macrochirus	Insectivore	Intermediate	No	1	☐
Cyprinidae	Clinostomus funduloides	Insectivore	Intermediate	Yes	3	☐
Cyprinidae	Cyprinella chloristia	Insectivore	Intermediate	Yes	5	☐
Cyprinidae	Cyprinella nivea	Insectivore	Intermediate	No	1	☐
Cyprinidae	Cyprinella pyrrhomelas	Insectivore	Intolerant	Yes	86	☐
Cyprinidae	Cyprinella zanema	Insectivore	Intolerant	No	2	☐
Cyprinidae	Nocomis leptocephalus	Omnivore	Intermediate	Yes	64	☐
Cyprinidae	Notropis hudsonius	Omnivore	Intermediate	Yes	59	☐
Cyprinidae	Notropis scepticus	Insectivore	Intermediate	No	3	☐
Cyprinidae	Notropis sp. cf. chlorocephalus	Insectivore	Intermediate	Yes	13	☐
Ictaluridae	Ameiurus brunneus	Insectivore	Intermediate	No	1	☐
Ictaluridae	Ameiurus platycephalus	Insectivore	Tolerant	Yes	17	☐
Ictaluridae	Noturus insignis	Insectivore	Intermediate	Yes	33	☐
Percidae	Etheostoma olmstedi	Insectivore	Intermediate	No	5	☐
Percidae	Etheostoma thalassinum	Insectivore	Intolerant	Yes	39	☐
Percidae	Percina crassa	Insectivore	Intolerant	No	2	☐

NCIBI Metrics

Metric	Value	Score
Number of Species:	21	5
Number Fish:	394	5
Number Darter Sp:	3	5
No. Sunfish,Bass,Trout:	3	5
Number Sucker Sp:	3	5
Number Intolerant Sp.	4	5
Percent Tolerant Fish:	13	5
Percent Omni + Herb:	31	5
Percent Insectivores:	69	5
Percent Piscivores:	0.00	1
Percent Diseased Fish:	0.76	3
Percent Sp Multiple Ages:	57	5

Exotics

Number Exotic Fish	0
Number Exotic Species	0

Notes

Collectors = DeBerardinis, Simonson, Tracy, Vander Borgh. Substrate = cobble, boulder, bedrock. Sampled 600 ft. upstream, beginning at high arched concrete culvert. No seine used, used green nets; if flow is sufficient seine would be very effective. Low gradient near the culvert (1st 100 ft.), high gradient with plunges (next 500 ft.). Plunge pools, chutes and riffles, soft bottom pool at the bridge. No Carolina Fantail Darter. One Sandbar Shiner, Rosyside Dace, and Spottail Shiner with popeye. Largemouth Bass represented only by young-of-year. Water easily silted.

SFCAP SOP Appendix 9. Web Links

Digital Pictures of Fish – The Southeastern Fishes Council (http://www.sefishescouncil.org/fishes/) and EFISH, the Virtual Aquarium, the Department of Fisheries and Wildlife Sciences, Virginia Polytechnic Institute and State University (http://www.cnr.vt.edu/efish/).

NC Division of Water Resources (NCDWR) -- http://www.ncwater.org/

NCDWR Basinwide Assessment Reports -- http://portal.ncdenr.org/web/wq/ess/reports

NCDWR Basinwide Planning -- http://portal.ncdenr.org/web/wq/ps/bpu

NCDWR Biological Assessment Branch -- http://portal.ncdenr.org/web/wq/ess/bau

NCDWR Intensive Survey Branch Standard Operating Procedure -- http://portal.ncdenr.org/web/wq/ess/isuf

NCDWR Stream Fish Community Assessment Program Raw Data -- http://portal.ncdenr.org/web/wq/ess/bau/ncibi-data

NCDWR Stream Fish Community Assessment Program NCIBI Scores and Ratings -- http://portal.ncdenr.org/web/wq/ess/bau/ncibi-scores

NCDWR Water Quality Standards -- http://portal.ncdenr.org/web/wq/ps/csu/swstandards

Native and Exotic Freshwater Fish in North Carolina -- http://portal.ncdenr.org/web/wq/ess/bau/nativefish

APPENDIX 5:

Field Meter Calibration Sheet

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Appendix 5. Field Meter Calibration Sheet

Water Quality Monitoring Field Meter Calibration Sheet

Collector(s):

Study:

Sampling Location:

Meter Model:

Meter / Sonde Serial No:

	Date yy/mm/dd	Time 24hr hh:mm	Initials
Pre-Sampling Calibration			
Post-Sampling Check			

Miscellaneous **(Does not apply to YSI or Accumet Meters)**

	Battery Level (V)		Stirrer Working?
Pre-Sampling Calibration			Y / N
Post-Sampling Check			Y / N

Battery Ranges = Surveyor: internal- 7.2-7.5V, external- 11-13V; Quanta: 4.0-4.5V

Barometer Calibration (mmHg)

**YSI Pro Plus Meters Only*

Initial Reading	Calibrated Value

Dissolved Oxygen (mg/L)

	Temp. °C	Initial % Saturation	Barometric Pressure (mmHg)	Altitude (ft.)	D.O. Table Value	Initial Meter Reading (mg/L)	Calibrated Meter Reading (mg/L)	Calibrated % Saturation
Pre-Sampling Calibration								
Post-Sampling Check								
					Within ± 0.5 ? Y / N			

Specific Conductance (µS/cm at 25°C)

	Dry Air [1, 2] Zero (0)		Lot #: Conductivity Standard [3] Value: _____		Lot #: Calibration Check Value: _____
	Initial Meter Reading	Calibrated [4] Meter Reading	Initial Meter Reading	Calibrated [4] Meter Reading	Initial Meter Reading
Pre-Sampling Calibration					
Post-Sampling Check	Within ± 2? Y / N		Within ±10%? Y / N		Within ±10% Y / N

±10% Ranges for Sp. Cond.

Standard	Range
100	90 to 110
500	450 to 550
1,000	900 to 1,100
10,000	9,000 to 11,000
15,000	13,500 to 16,500
50,000	45,000 to 55,000

NOTE: Quanta reads in mS/cm; move decimal 3 places right for µS/cm.

[1] Dry Air CALIBRATIONS are conducted for 4a and MS5 Hydrolabs only.

[2] Dry Air CHECKS (confirmation of zero in dry air) are conducted for YSI 85, YSI 6920, YSI Pro Plus & Quanta meters.

[3] Conductivity standards are used to CHECK the YSI 85 meter and to CALIBRATE all Hydrolab meters and the YSI 6920 & YSI Pro Plus.

[4] Does not apply to Dry Air CHECKS or Conductivity Standard CHECKS (leave blank).

pH (SU)

	Lot #: Buffer #1 7.0 Buffer Temp: _____		Lot #: Buffer #2 4.0 / 10.0 Buffer Temp: _____		Slope Efficiency[5]	Confirmation Buffer 7.0
	Initial Meter Reading	Calibrated Meter Reading	Initial Meter Reading	Calibrated Meter Reading		Meter Reading
Pre-Sampling Calibration						
Post-Sampling Check	Within ± 0.2? Y / N		Within ± 0.2? Y / N			Within ± 0.1? Y / N

[5] Slope efficiency applies to Accumet meters only (does not apply to Hydrolab or YSI meters).

Comments:

Keep original on file for 5 years

Ver. 06/05/2012

APPENDIX 6:

YSI PROFESSIONAL PLUS GUIDANCE TABLES

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DISSOLVED OXYGEN

YSI PRO PLUS with POLARGRAPHIC SENSOR

CALIBRATION

D.O. Calibration for YSI Meters with Polargraphic Sensor:

All calibrations should be performed in a controlled environment. Field calibrations are not recommended.

I. BAROMETER CALIBRATION

Access the Barometer Calibration Menu:

1) Press **Cal** key, highlight **Barometer,** and press **Enter**.
2) Highlight **mmHg**, and press **Enter**.
3) Highlight **Calibration Value**, and press **Enter.** Input the "true" barometric pressure (mmHg). Highlight **<<<Enter>>>,** and press **Enter**. *True barometric pressure is listed on the Dissolved Oxygen Table for your corresponding regional office.*
4) Wait for readings to stabilize. Record displayed value as "Initial Reading" in the "Barometer Calibration" section of the calibration sheet.
5) Highlight **Accept Calibration** and press **Enter** to calibrate Barometric Pressure.
6) "`Calibrating Channel...`" and then "`Saving Configuration...`" will be displayed at bottom of calibration screen before returning to the main screen.
7) Record displayed value as "Calibrated Value" in the "Barometer Calibration" section of the calibration sheet.

II. (% AIR CALIBRATION IN WATER-SATURATED AIR)

8) Remove calibration storage cup from sonde. Confirm D.O. probe has been stored in moist environment. Place calibration cup on work surface with uncapped end facing upward.
9) Use lens tissue to carefully dry all sensors. Temperature and D.O. sensors must be completely dry.
10) Pour small amount of tap water into calibration cup (approximately 1/8" - just enough to completely cover the bottom of the calibration cup and create a 100% humid environment). Temperature and D.O. sensors CANNOT be in contact with water during calibration.
11) Carefully place probes (pointing downward) into calibration cup so that no water gets on the temperature or D.O. sensor.
12) Twist calibration cup onto sonde **no more than 1 or 2 threads**, so the cup is able to vent to the atmosphere.
13) Wait at least 15 minutes for D.O. sensor to stabilize.
14) Record the following values on calibration sheet: "Temperature", "Initial % Saturation", and "Initial Meter Reading (mg/L)".
15) Use the *Dissolved Oxygen Table* for your location to find the "D.O. Table Value" (based on the temperature displayed on the meter), and record value on calibration sheet.

Access the D.O. Calibration Menu:

16) Press **Cal** key, highlight **DO,** and press **Enter**.
17) Highlight **DO%**, and press **Enter**.
    NOTE: Dissolved oxygen should always be calibrated using % saturation.
    Calibrations based on "mg/l" require a water sample with a known D.O. concentration (requires Winkler titration).
18) In the "Dissolved Oxygen" section of the calibration sheet, record the "Barometric Pressure" displayed on the meter and the altitude for your location (provided on regional office *Dissolved Oxygen Tables*).
19) Highlight **Accept Calibration** and press **Enter** to calibrate Dissolved Oxygen.
    "`Calibrating Channel...`" and then "`Saving Configuration...`" will be displayed at bottom of calibration screen before returning to the main screen.
20) On the calibration sheet, record the displayed mg/L value as "Calibrated Meter Reading" and the DO% value as the "Calibrated % Saturation" value.

    *** NOTE: The "D.O. Table Value" and the "Calibrated Meter Reading" value should be within ±0.5 mg/L of each other.**

Terminal Calibration Check (Post-Sampling Meter Check)

NOTE: Barometric pressure is not checked or recalibrated post-sampling.

a. Repeat calibration steps 8 thru 13. Record "Temperature", "% Saturation", "Initial Meter Reading".
b. Record the barometric pressure and altitude for the location post-sampling checks are being performed.
c. Repeat calibration step 15.
d. The post-sampling "D.O. Table Value" and the post-sampling "Initial Meter Reading" should be within ±0.5 mg/L of each other.

MAINTENANCE

Cracked Probe:

If meter readings are unusual and calibrating the meter does not correct the issue, check the condition of the D.O. probe – sometimes a crack can develop in the plastic along the side of the probe. Cracked probes should be replaced immediately.

Probe Storage:

Store probe in Calibration/Storage Cup with a small of tap water to create a 100% saturated air environment.

During storage, probes should not be submerged in water.

Do not use distilled water (this will damage the pH probe).

During long-term storage, inspect at least once a month to ensure the probe is still in a moist environment.

D.O. Membrane Replacement (YSI 5908- Yellow Teflon):

Replace electrode solution and membrane at least every 30 days during regular use or if: bubbles are visible under membrane; significant deposits of dried electrolyte are visible on membrane; calibration is impossible; readings are erratic or unstable; or membrane is damaged.

1) Remove and discard old membrane cap.
2) Rinse sensor tip with distilled or deionized water.
3) Prepare electrolyte solution (Na_2SO_4, KCl) according to the directions on the bottle (included in Membrane Cap Kit). Newly prepared solution must sit for 1 hour before using to prevent air bubbles under the membrane.

   When a new electrolyte solution is prepared, record preparation date (in permanent ink) on the side of the solution bottle. Discard electrolyte solutions 12 months after the recorded preparation date.
4) Fill new membrane cap half-full with electrolyte solution. Do not touch membrane surface. Tap side of cap lightly to release bubbles.
5) Screw membrane cap onto probe (small amount of electrolyte should overflow).
6) Re-attach probe sensor guard.

Cleaning Dirty, Tarnished Silver Anode and Gold Cathode:

SANDING AND CLEANING THE ELECTRODE ARE NOT PART OF THE ROUTINE MAINTENANCE AND SHOULD ONLY BE PERFORMED WHEN ABSOLUTELY NECESSARY! If performed too frequently, the electrode will be destroyed!

1) Remove membrane and soak probe overnight in 3% ammonium hydroxide (NH_4OH).
2) Rinse sensor tip with deionized water.
3) Use 400 or 600 grit wet/dry sandpaper to clean and polish the anode and cathode – no more than 3 to 4 twists of the sandpaper should be sufficient to remove any deposits or tarnish.
4) Rinse heavily with deionized water.
5) Install new membrane.
6) Turn meter "ON" and allow unit to stabilize for at least 30 minutes to 3 hours before calibrating.

May take several hours for the meter to stabilize.

SPECIFIC CONDUCTANCE

YSI PRO PLUS

CALIBRATION

THREE-STEP SPECIFIC CONDUCTANCE PROCEDURE:

I. "DRY AIR" (ALWAYS ZERO):

The "Dry Air" step is a **check** for YSI meters.

1) Attach calibration cup to probe. Fill cup half-full with deionized water and seal with lid. Shake probe to rinse.
2) Remove calibration cup. Place cup on work surface with the uncapped end facing upward.
3) Use a cotton swab to dry the inside of the conductivity cells.
4) Record displayed value as "Initial Meter Reading" in the "Dry Air" section of the calibration sheet. The probe should read close to zero (± 2).

   If the reading is not within ± 2, follow cleaning procedure, and repeat calibration procedure.

II. CONDUCTIVITY STANDARD:

Calibrations should be performed using a **fresh, certified** conductivity standard that is similar to the conductivity of the samples to be collected that day. Record the standard's "true value" (found on the certificate of analysis or bottle label) and lot number (also called analysis number) on the calibration sheet. Traceable® Certificate of Analysis for Conductivity Solution sheets (one certificate for each lot number) should be retained and stored in a notebook.

5) Re-attach calibration cup. Fill cup half-full with deionized water. Seal cup with lid and shake probe to rinse. Discard rinse water.
6) Rinse sensors with small amount of conductivity standard. Discard rinse.
7) Pour fresh conductivity standard (≥1000 µS/cm) into the calibration cup. Make sure there is enough standard to cover the entire conductivity cell and temperature sensor when the probe is placed in the cup.
8) Tap or agitate sonde to remove air bubbles trapped in the conductivity cells. Air bubbles will result in erroneously low readings.
9) Press **Cal** key, highlight **Conductivity**, and press **Enter**.
10) Highlight **Sp. Conductance** and press **Enter**.
11) Highlight **SPC- uS/cm** and press **Enter**.
12) Highlight **Calibration Value** and press **Enter**. Input the True Value of the conductivity standard in **microSiemens/cm (µs/cm)**. Highlight **<<<Enter>>>**, and press **Enter.**
13) Wait for readings to stabilize. Record displayed value as "Initial Meter Reading" in the "Conductivity Standard" section of the calibration sheet.
14) Highlight **Accept Calibration** and press **Enter** to calibrate meter.
    "`Calibrating Channel...`" and then "`Saving Configuration...`" will be displayed at bottom of calibration screen before returning to the main screen.
15) Record displayed value as "Calibrated Meter Reading" on calibration sheet.

    Never accept an out-of-range calibration (flagged by an error message on the meter).

III. CALIBRATION CHECK:

16) Rinse with deionized water and wipe dry with a lens tissue or a lint-free cloth.
17) Confirm that the meter display is reading 0 (zero) µS before going to the next step.
18) Repeat steps 5-8 with a conductivity standard of a value different from the one used in the previous calibration steps. Choose a standard that will give the best range of values for the anticipated samples to be collected.
19) Record SpCond value as "Initial Meter Reading" in the Calibration Check section on the calibration sheet. The value must be within 10% of the standard.

Terminal Calibration Check (Post-Sampling Meter Check)

a. Repeat calibration steps 1 thru 4, and record value in the "Dry Air" section on the calibration sheet.
   For the "Dry Air" check, displayed value should be between -2 and 2 µS.
b. Repeat calibration steps 5 thru 8. Record value in the "Conductivity Standard" section on the calibration sheet.
   "Conductivity Standard" value should be within ±10% of the standard.
c. Repeat steps 16-19, and record value in the "Calibration Check" section on the calibration sheet.
   "Calibration Check" value should be within ±10% of the standard.

SPECIFIC CONDUCTANCE

YSI PRO PLUS

MAINTENANCE

✱ **Never accept an out-of-range calibration**! (flagged by an error message on the meter display)

Checking the Conductivity Cell Constant:

When troubleshooting the conductivity probe, first check the cell constant.

1) Press **Folder** Key. Highlight **View GLP**, and press **Enter**. Scroll to most recent conductivity calibration to view the Cal Cell Constant.
2) The value displayed next to "`Cal Cell Constant`" should be 5.0, ± 0.45.
   Numbers outside of this range indicate a problem in the calibration process or that a contaminated standard was used to calibrate the meter.
3) If conductivity cell constant is not within the acceptance range (between 4.55 and 5.45), clean the cell, and reset the calibration cell constant (see instructions below).

Cleaning Conductivity Sensor:

Conductivity cell should be rinsed with deionized water after field use.

Clean conductivity cell frequently. A clean cell is imperative for accurate readings.

1) Dip small cleaning brush (provided with new meters) into distilled or deionized water and insert brush into each hole 15-20 times. For a more thorough cleaning, use a mild liquid or foam dishwashing detergent with the brush.
2) Rinse sensor thoroughly with deionized water.
3) Perform the Dry Air Check described in Calibration Steps 1-4 to ensure probe reads close to zero in air.

Reset Calibration Cell Constant:

Reset the calibration cell constant by accessing the Calibrate menu:

1) Press **Cal** Key, highlight **Restore Default Cal,** and press **Enter**. Highlight **Conductivity**, and press **Enter.**

2) The menu will ask **"Are you sure you want to remove the current user calibration parameters for this channel?"** Highlight **Yes**. Press the **Enter** key.

3) Recalibrate the meter using fresh, certified conductivity standards.

CALIBRATION

Two-point pH Calibration Required (Three-point pH Calibration is Optional):

1ST CALIBRATION POINT (ALWAYS START WITH 7 BUFFER):

1) Rinse probes and calibration cup with distilled water.
2) Rinse probes and calibration cup with small amount of 7 pH buffer. Discard buffer rinse.
3) Fill calibration cup with enough **fresh** 7 pH buffer to cover the pH glass bulb and temperature sensor.
4) Check temperature of pH buffer. Record value on calibration sheet.

   Note: If the temperature at which you are calibrating is significantly different from 25° C, check the buffer bottle for the corrected pH value at the corresponding temperature (the corrected pH value will be used in step 7).
5) Press **Cal** key. Highlight **ISE1 (pH)** and press **Enter**.
6) The prompt "`Ready for point 1`" will appear briefly at the bottom of the screen. Check Calibration Value. If value is correct, go to Step 7. If value is incorrect, highlight **Calibration Value** and press **Enter**. Input 7.0 (or, if applicable, the corrected pH value from step 4). Highlight **<<<Enter>>>**, and press **Enter.**
7) Actual-time readings will be displayed. When readings have stabilized, record displayed actual pH value as "Initial Meter Reading" for Buffer # 1 on calibration sheet.
8) Highlight **Accept Calibration**, and press **Enter** to calibrate.
9) "`Ready for Point 2`" will be displayed at the bottom of the screen very briefly. Record displayed pH calibration value as "Calibrated Meter Reading" for Buffer #1.

NOTE: IF YOU ACCIDENTALLY LEAVE THE pH CALIBRATION MENU BEFORE CALIBRATING YOUR 2ND POINT, YOU MUST START OVER BECAUSE THE 1ST CALIBRATION POINT WAS NOT COMPLETED. "Calibrate ISE1 (pH)" should still be displayed at the top of the screen. Remain on the same display screen as in Step 9 in order to see the actual-time temperature reading for the 2nd buffer.

2ND CALIBRATION POINT:

10) Rinse probes and calibration cup with distilled water.
11) Rinse probes and calibration cup with small amount of 2nd buffer (either 4 or 10 pH buffer). Discard buffer rinse.
12) Fill calibration cup with enough **fresh** buffer to cover the pH glass bulb and temperature sensor.
13) Actual-time readings will be displayed. When readings have stabilized, record the temperature reading.

    Note: If the temperature at which you are calibrating is significantly different from 25° C, check the buffer bottle for the corrected pH value at the corresponding temperature (the corrected pH value will be used in step 14).
14) Check Calibration Value. If value is correct, go to Step 15. If value is incorrect, highlight **Calibration Value** and press **Enter**. Input correct buffer value (or, if applicable, the corrected pH value from step 13). Highlight **<<<Enter>>>**, and press **Enter.**
15) Actual-time readings will be displayed. When readings have stabilized, record displayed actual pH value as "Initial Meter Reading" for Buffer # 2 on the calibration sheet.
16) Highlight **Accept Calibration** and press **Enter** to calibrate.
17) "`Ready for Point 3`" will be displayed briefly at the bottom of the screen. If only performing a 2-point calibration, press **Cal** Key to complete calibration process.
18) Record displayed pH value as "Calibrated Meter Reading" for Buffer #2.

If you chose to do a "`3-point calibration`", do NOT press **Cal** key in step 17 and repeat steps 10 through 17 using the 3rd buffer.

CONFIRMATION BUFFER: CONFIRMATION BUFFER STEP IS VERY CRITICAL FOR THE YSI PRO PLUS – DO NOT SKIP IT!

20) Rinse probes and calibration cup with distilled water.
21) Rinse probes and calibration cup with small amount of 7.0 pH buffer. Discard buffer rinse.
22) Fill the calibration cup with enough **fresh** buffer to cover the pH glass bulb and temperature sensor.
23) Wait 1 to 3 minutes for pH readings to stabilize.
24) Record the displayed pH value as the "Meter Reading" under "Confirmation Buffer 7.0" on the calibration sheet
25) Confirm that the "Meter Reading" value is within ± 0.1 of the buffer value (between 6.9 and 7.1).

Terminal Check (Post-Sampling Meter Check)

a. Repeat steps 20 thru 23 (for 7 buffer); record displayed value on calibration sheet. Value should be within ±0.2 of 7.0.
b. Repeat steps 20 thru 23 for Buffer #2. Record value on calibration sheet. Value should be within ±0.2 of Buffer #2.

pH — YSI PRO PLUS

MAINTENANCE

✶ **Never accept an out-of-range calibration**! (flagged by an error message on the meter display)

Indicators that maintenance is needed:
Difficulty calibrating pH sensor, slow response, erratic readings, clogged or black reference junction, coated glass bulb.

Probe Storage:

Do NOT allow the pH sensor to dry out! Sensors that have dried out may be permanently damaged!

Store probe in calibration/storage cup filled with 1/8" of tap water (never use distilled water to store probe).

If probe will not be used for several months, remove probe and store in pH 4 buffer. Seal the vacant port with a port plug.

Probe Lifespan:

The pH probe has a lifetime of approximately 12-24 months (in some cases, probes may last 3+ years).

When troubleshooting pH sensor problems, start by checking age of probe and replace as-needed:
On the side of each probe is the imprint "YSI 1001" followed by 2 numbers and a letter. The 2 numbers and the letter indicate the year and month in which the probe was made. For instance, 07D means the probe was made in April, 2007. (i.e. A=Jan, B=Feb, etc.).

Troubleshooting with mV readings:

1) Follow steps for pH calibration. During calibration, record pH mV values from the "Calibrated" screen for each buffer.
2) Evaluate the pH mV values:
   The span or "slope" between the pH 4 and pH 7 and between pH 7 and pH 10 should be approximately 165 to 180 mV.
   pH 7 should be 0 mV ± 50 mV. pH 4 should be 180 mV ± 50 mV. pH 10 should be -180 mV ± 50 mV.
   Example: If a probe reads +10 mV in pH 7 buffer, then the probe should also read between 175 and 190 mV in pH 4 buffer, and between -155 mV and -170mV in pH 10 buffer.
3) If the mV values fall outside the range of 160-180 mV, the probe should be replaced soon.
   Note: The probe will no longer calibrate when the span is outside of the range of 150-210 mV.

General pH Probe Cleaning:

Use deionized water and a soft lens cloth or a cotton swab to remove foreign material from the glass bulb. If good response is not restored, perform the following procedure:

1) GENTLY clean the glass bulb and white probe face by carefully rubbing a cotton swab soaked in mild dishwashing detergent. Apply little to no pressure, as the glass bulb is very thin and fragile!
2) Rinse probe thoroughly with deionized water.
3) Wipe probe with cotton swab that has been saturated with water. Rinse probe again.

Advanced pH Probe Cleaning and Restoration:

The need and frequency depend on the type of surface water being monitoring.

The probe must be removed from the sonde before advanced cleaning.

To remove more resistant deposits and biological growth, use HCl acid and bleach.

To perform an advanced cleaning, refer to the Care, Maintenance, and Storage section of the YSI Professional Plus User Manual.

Reference Junction:

The reference junction is a small tab located between the edge of the white surface of the pH probe face and the gray raised area around the pH probe face.

When new, the junction will be an off-white color.

As it ages, the junction will become darker.

A black reference junction coupled with slow response and/or erratic readings indicates a more advanced cleaning may be needed.