Department of Environmental Conservation Laboratory
UVM
Hills Building – D.E.C. Laboratory
105 Carrigan Drive
Burlington VT 05405

Quality Assurance Plan

2015

Dan Needham **March 2015**
Interim QA Officer, DEC Laboratory
802-585-9808

T. Guy Roberts **March 2015**
Laboratory Director
802-522-3502

Revision 22 Note:

Volatile organic methods for air, water, and soil are mostly back online after the transition to the Hills building at the University of Vermont campus. Semi-volatiles analyses are still offline. This revision still has all references to these methods in hopes of bringing them back on-line in the near future.

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2.0 Introduction

The Vermont DEC Laboratory Quality Manual documents or references documents that describe the Department of Environmental Conservation (DEC) Laboratory policies and procedures as required by The NELAC Institute – TNI and the U.S. E.P.A. Region I Quality Assurance Office. The manual is reviewed by our TNI accrediting authority which is the New Hampshire Environmental Laboratory Accreditation Program (NHELAP) and US EPA Region 1 prior to the laboratory's biannual on-site audit. The manual can be accessed online at http://www.anr.state.vt.us/dec/lab/htm/quality control.htm

2.1 Objectives and Commitments of Management

The Vermont Department of Environmental Conservation relies on its Laboratory to provide data, which is the scientific basis for its program decisions. The Department's management is committed to provide the necessary resources to insure the Laboratory can produce high quality data and implement all TNI requirements.

Management's Quality System Policy Statement

The Department of Environmental Conservation Laboratory is committed to providing consistent, high quality data in a timely manner. Since each analytical result will be used by the client to make an important program decision, each analytical result is of critical importance. It is imperative that the DEC Laboratory generate and report data of known quality. Through our Quality Assurance Plan (QAP) we have outlined for our clients all procedures and precautions taken to insure that reported data is consistently of high quality. DEC's commitment to maintain the Laboratory's quality objective is demonstrated by the following:

1. An expertly staffed and fully equipped laboratory facility
2. Successful participation in multiple TNI, USGS and NWRI approved proficiency testing studies.
3. Successful implementation of a TNI compliant quality system.
4. Annual internal audit with management review of each analytical center.
5. Timely reporting of analytical results.
6. Laboratory test results which are supported by quality control data and documented testing procedures.
7. Systems to inform the client if analytical data does not meet all quality control requirements.

This policy is communicated to new employees and is constantly reinforced to all employees. It is implemented and maintained by employees at all levels. This policy is documented by management through employee evaluations, by requiring documentation of formal reviews of the QAP and all revisions, training procedures, internal audits and document control.

2.2 Employee Code of Ethics, Training, and Reporting of Unethical Behavior

2.2.1 Employee Code of Ethics and Laboratory Fraud

Laboratory fraud is defined as: The deliberate falsification of analytical data or quality control results, where failed methods and contractual requirements are made to appear acceptable. The Vermont DEC Laboratory management recognizes that employee ethics have a profound effect on the integrity and quality of the work performed at the Laboratory.

Policies regarding the acceptable handling, reporting and review of data are outlined in the Laboratory Quality Assurance Plan (QAP) and Laboratory Standard Operating Procedures (SOPs). Improperly performed procedures including all steps in calibration, analysis and data reporting, are not tolerated. Examples of unacceptable procedures include: falsifying data, improper data manipulations, adjustments of instrument clocks, inappropriate changes in concentrations of standards, misrepresenting quality control data, manipulation of computer software, data file substitution and concealment of known problems or unethical behavior or action from laboratory management and/or clients. Specific examples of unethical conduct are outlined in the training document, "Preventing Improper Laboratory Practices", Advanced Systems, Inc

Laboratory employees must conduct themselves in an honest and ethical manner at all times and must remain free of commercial or financial pressure which might influence their technical judgment.

2.2.2 Ethics Training

The State of Vermont Agency of Natural Resource Human Resources Office provide all new full time employees with State of Vermont Policies and Procedure. Each new employee must complete the *New Employee Orientation* Program that includes policy on conflicts of interest. Records are maintained with the Personnel Administrator.

New Laboratory personnel must also complete an orientation program at the DEC Lab. Documentation is kept in Laboratory training files that states that new employees have read, understood and will use the latest version of the Laboratory's QAP and Laboratory SOPs which relates to his/her job responsibilities. Documents that must be read include:

- Laboratory Quality Assurance Plan (QAP)
- Relevant Laboratory Standard Operating Procedures (SOPs)

Annual ethics refresher training is required for each employee. Documentation of the training material presented is retained. Each employee must sign a form that states that they understand their obligations related to data integrity. The form is retained in ethics training folder in the QA/QC cabinet. The refresher training focuses on issues arising from activities such as hiring, training and supervising staff; handling, analysis and reporting of quality assurance data and legal responsibilities including the potential punishments and penalties for improper, unethical and illegal actions. Annual training reinforces the policies and procedures outlined in the Laboratory QAP and SOPs. Training may be conducted internally or by an outside source.

2.2.3 Reporting of Unethical Behavior

Employees are required to report any suspected unethical activities to Laboratory management. The reporting can be in writing or verbal. Unethical situations can be reported anonymously through the interoffice mail system. Reporting can be to the Laboratory Director, Supervisor, QA Officer or technical director of an analytical center. It then becomes the responsibility of that individual to initiate corrective actions which may include reporting the incident to upper management or the Department of Personnel. Each employee involved in the reporting and receiving of reported information must document the incident, actions taken, information reported and individual the incident was reported about and reported to. This ensures that the individual reporting any suspected unethical behavior has evidence that they have acted appropriately.

All investigations resulting from data integrity issues should be conducted in a confidential manner until they are completed. These investigations shall be documented, as well as any notifications made to clients receiving any affected data.

2.2.4 Management Review of Data Integrity Procedures

Management shall annually review and update as needed data integrity procedures. Procedures are documented in the Laboratory's QA Plan and SOPs. The QA Officer is responsible for annual QA Plan revisions and Technical Directors are responsible for the review and revision of SOPs. Revisions are reviewed and signed by the Laboratory Supervisor.

3.0 Laboratory Review of Requests for Testing

3.1 Project Plans

The U.S. EPA requires that a satisfactory Quality Assurance Project Plan (QAPP) be submitted to EPA's Quality Assurance Office for any project funded in whole or in part by EPA. The Department/Agency supports this policy for projects funded in part or whole by state funds. Planning is a critical component for successful projects. The information in Quality Assurance Plans allows EPA, state project officers, and Laboratory staff to review all technical and quality aspects of a project including planning, implementation, documentation and assessment. The QAPP must document the type, quantity and quality of data needed to support environmental decision making. Project plans allow Laboratory staff an opportunity to review project expectations and determine if the Laboratory has the equipment and resources available to meet data quality expectations.

This EPA approved Laboratory Quality Assurance Plan (QAP) is designed to assist Laboratory users in the preparation of Quality Assurance Project Plans (QAPP). Vermont environmental programs needing to meet EPA's and State requirement for a QAPP can reference the Laboratory QAP. If quality assurance objectives listed in this document do not meet project requirements the Laboratory should be contacted. In some instances routine Laboratory protocols can be modified to meet quality objectives.

EPA New England's systematic implementation approach for QAPPs is described in *EPA New England Quality Assurance Project Plan Program Guidance*; January 2010 (Rev 2). http://www.epa.gov/Region1/lab/qa/pdfs/QAPPProgram.pdf. The guidance provides region-specific implementation information and program-specific guidance. The U.S. EPA Region 1 QAPP contact is Nora Conlon, (conlon.nora@EPA.gov). The EPA encourages QAPP writers to contact the Region 1 office with questions prior to initiating a QAPP. The following documents and web sites may be useful.

Program	Guidance
General	*EPA New England Quality Assurance Project Plan Program Guidance,* January 2010 (Rev 2). http://www.epa.gov/Region1/lab/qa/pdfs/QAPPProgram.pdf *EPA Guidance for Quality Assurance Project Plans*(EPA QA/G-5), December 2002, EPA/240/R-02/009, http://www.epa.gov/quality/qa_docs.html
Water Quality Monitoring	*The Volunteer Monitor's Guide to Quality Assurance Project Plans,* September 1996, EPA/841/B-96/003, http://epa.gov/owow/monitoring/volunteer/qapp/vol_qapp.pdf
Wadeable Streams and Rivers	*Generic Quality Assurance Project Plan Guidance for Programs Using Community Level Biological Assessments in Wadeable Streams and Rivers*, http://www.epa.gov/bioindicators/html/qapp.html
Brownfields	*Planning and Documenting Brownfields Projects: Generic Quality Assurance Project Plans, and Site specific QAPP Addenda*

	http://www.epa.gov/ne/lab/qa/pdfs/PlanDocBrownfields.pdf http://www.epa.gov/ne/lab/qa/pdfs/PlanDocBrownfieldsappendAB.pdf *Quality Assurance Guidance for Conducting Brownfields Site Assessments,* September 1998, EPA 540-R-98-038, http://www.epa.gov/swerosps/bf/pdf/bfqag4.pdf
Hazardous Waste (Federal Facilities, Superfund and RCRA)	*Uniform Federal Policy for Quality Assurance Project Plans,* July 2004, OSWER Directive http://www.epa.gov/fedfac/pdf/ufp_manualv1_july04.pdf
Air	Ambient Monitoring Technology Information Center http://www.epa.gov/ttn/amtic/
Pesticides	*Guidance for Quality Assurance Project Plans-Development for EPA Funded Cooperative Agreements with State and Tribal Agencies for the Conduct of FIFRA Pesticide Programs,* December 15, 2000 http://www.epa.gov/region9/qa/pdfs/finalqaappver9.pdf

3.2 Lab Contracting Policy

For programs (customers) submitting samples for Lab analysis the following items are discussed to ensure that the lab policy and procedures are understood and the laboratory has the capability and resources to meet the client's requirements.

1. Tests, requested method(s) to be used, required reporting limits.
2. Turn around times.
3. Enforcement administrative procedures required (Y/N).
4. Method of sample delivery.
5. Client and Laboratory responsibilities for sample preparation.
6. Lead time needed to schedule sample delivery and to secure sampling bottles.
7. Analytical method used. Existing methods have demonstration of ability documentation in place. New procedures will require method development and an initial demonstration of ability documentation prior to samples being accepted.
8. Laboratory input on applicability of methods to the type of sampling planned.
9. Report deliverables.

The Laboratory's TNI accreditation status is posted on the Laboratory's web site under Laboratory Documents, (Rate Sheet and NELAC Accreditation Status). The final agreement will notify the client if the Laboratory possesses the necessary resources to meet the client's project needs. Prior to the initiation of any work any differences between the original requests and the final contract specifications must be resolved. The Laboratory must notify the client in writing if the Laboratory's TNI status changes during the life of the contract or if the contract needs to be amended after work has commenced. See policy on non-conforming work (Section 15.2).

3.3 Subcontracting of Analytical Work

A contract for laboratory analytical services will give State programs the ability to receive analytical services for parameters that the State's Environmental laboratory are unable to perform at this time or needs assistance to relieve sample backlogs.

Analytical results should be in a format compatible with Excel so it can be uploaded into the State's Laboratory Information Management System (LIMS). If requested, contractor will provide the raw data for a given test. The contractor must comply with the National Environmental Accreditation Program (NELAP) standards. Sample handling, preparation, and testing must be consistent with the contractor's applicable laboratory standard operating procedures (SOPs) and quality assurance plans. Practical Quantification Limits (PQLs) or equivalent, for each analyte, must be at or below those listed in this QAP, unless another PQL, or equivalent, for a given analyte(s) is agreed upon in writing by the "State" and the "Contractor."

4.0 Laboratory Organization and Responsibility

The DEC Laboratory is an internal service organization, which is charged with providing analytical support to programs in the Department of Environmental Conservation. The Department of Environmental Conservation (DEC) Laboratory is located within the State of Vermont Agency of Natural Resources and is administratively attached to the Commissioner's Office (Figures 4.1 and 4.2). The Laboratory provides a full compliment of analytical services to programs within the Department, other Departments within the Agency of Natural Resources, other State departments needing environmental analysis, and publicly funded non Agency programs. Frequently, Laboratory services are custom-tailored to meet user's individual needs and changing programmatic demands. Annual services provided by the Laboratory exceed 8,000 samples which equates to more than 20,000 analytical test results (FY 2010 figures). Organizationally the Chemistry Laboratory is separated into an administrative center and three analytical centers:

The Metals Analysis Center is responsible for analyzing metals in a wide variety of matrices. It supports a number of Departmental programs including acid rain, landfill assessment, hazardous waste investigations and lake sediment/fish studies. The center employs ICP/MS, ICP and a mercury cold vapor system as the methods of analysis.

The Inorganic Chemistry and Microbiology Center is responsible for all non metal/inorganic analyses performed at the Laboratory. The center supports a number of diagnostic water quality studies, landfill assessments, Departmental investigations and swimming water testing. Analyses are performed using auto analyzers, ion chromatography, and a variety of manual chemistry and microbiology methods.

The Organic Chemistry Center provides identification for organic materials in water, solids and air. Analyses include volatiles, carbonyls and motor/diesel range organic chemicals. Analyses are performed using gas chromatography, gas chromatography-mass spectroscopy and high performance liquid chromatography.

The Laboratory analytical centers require considerable administrative support, including a Laboratory supervisor, secretary, personnel to manage the safety and quality assurance plans, data review and approval, Laboratory technicians that assist in managing glassware, bottle orders and simple analyses.

Environmental scientists are assigned permanently to an analytical center but will assist in other centers of the Laboratory when needed. Technical Directors are responsible for all aspects of analysis within their center: instrument control, technical method development, equipment purchases, quality control, supervision and training of seasonal technicians and workload management. Technicians assist in work centers as work loads require. Position descriptions outlining education and experience requirements are available upon request.

In order to ensure that data are of acceptable quality, all data is subject to review. The Laboratory data review process is described in Section 10.2. Individuals responsible for ensuring data are valid, and for routinely assessing measurement systems for precision and accuracy are listed below.

4.1 Laboratory Users

4.1.1 Program Directors, Project Leaders

- Responsible for providing the Laboratory and EPA (federally funded projects) with a QA Project Plan which identifies and defines data quality needs in terms of appropriate analytical levels; contaminants and levels of concern; required detection limits; critical samples; and completeness, comparability and representativeness requirements.
- Responsible for scheduling the collection of additional samples to assess precision for matrices the Laboratory has not routinely analyzed and collecting appropriate field quality control samples (Section 11.1).
- Reviews data as it becomes available. Contacts Laboratory if questions arise.
- Oversees the sampling process to ensure field personnel are following proper sample collection and preservation steps.
- Responsible for providing written standards on operating procedures for all aspects of field work.
- Periodically assess data and initiates corrective action when analytical results do not provide useable data i.e. quantitation level is unacceptable for a particular set of low level samples; unacceptable field duplicate, filter or field blanks, split sample or equipment blank results or data does not conform to required accuracy, precision or completeness requirements.
- Notifies the Laboratory when Chain of Custody (COC) will be required on a sample set, preferably before the sampling event.
- Responsible for maintaining proper sample handling, and delivery of COC samples.

4.2 Laboratory Positions and Job Duties

4.2.1 Laboratory Director

- Assures that the Laboratory has sufficient personnel having the necessary education, training and technical knowledge and experience for their assigned duties.
- Assures that the Laboratory has appropriate equipment and supplies.
- Assures that the Laboratory has the capacity, facility and resources to perform new work.
- Acts as liaison between Laboratory and regulatory agencies (EPA) and Laboratory users.
- Oversees the transformation of analytical data which may be necessary to meet program needs.
- Evaluates periodic summaries of quality assurance data provided by the Quality

Assurance (QA) Officer and determines when data quality is unacceptable.

4.2.1 Environmental Scientist VI - Laboratory Supervisor

- Responsible for the overall technical quality of the work performed in the Laboratory and for assuring the use of standard methods.
- Supervises all personnel employed by the Laboratory.
- Responsible for ensuring that Laboratory employees are compliant with TNI standards.
- Oversees the Scheduling of projects and the completion of tasks within the required time schedule and sample hold times. Monitors progress of projects and communicates with Laboratory staff and users as required.
- Provides technical assistance to Laboratory users in regard to the selection of appropriate analytical and/or sampling methods and may review QA Project Plans submitted to the Laboratory.
- Provides technical assistance to Laboratory staff regarding QA problems and method and instrument selection.
- Reviews Laboratory standard operating procedures and insures that staff revise and update the documents as required.
- Reviews all data before it is reported as final and assures that results from different parameters of a sample correlate.
- Assures that the quality of all data reported by the Laboratory is documented.
- May participate in internal bench audits initiated by the QA Officer.
- Maintains the supply of sample bottles used for sample collection.
- Oversees the Chain of Custody (COC) sample transfer into the Laboratory and assures that data handling and COC records are organized and accessible

4.2.2 Environmental Technician III – Administrative Services Coordinator

- Daily oversight of administrative operations within the Laboratory, works directly with Laboratory Director in regard to human resources, purchasing, budgeting, lab production documentation. Is the main contact with lab users assisting with management of their sampling programs in re: to the Lab processes.
- Works directly with DBA to maintain the daily operation of the Laboratory data management system, which may include training of users / staff, updating data base with client information, programs, assist lab users / staff with any LIMS issues and work to get them corrected.
- Responsible for maintaining chain-of-custody and other pertinent data tracking forms within the laboratory.

- Assists clients with Sample log-in questions and assists in identifying and correcting sample log-in errors; trains lab users on use of LIMS.
- Works directly with QA Officer maintaining the QA process within the Lab.
- Laboratory Web page Administrator –maintains web page content; works directly with ANR Web Master.
- Manages the Lab equipment insurance program for Lab equipment.
- Manages the pre-log-in and distribution of labels and forms for volunteer monitoring projects. Coordinates and communicates with the Project Managers and responds to questions regarding log-in procedures.
- Prepares invoices and maintains record of invoice & receipts, work directly with Business Manager maintaining Lab accounts, etc.
- Creates production reports of Laboratory output.
- Maintains sampling plans and schedules for lab users.
- Oversees management of Laboratory contracts.
- Responsible for placing orders and tracking the status of all consumable supplies ordered by lab staff.
- Acts as Records Liaison Officer for the Laboratory.
- Works with BGS Purchasing & Contracting staff to develop purchasing contracts / BDAs with vendors that the Lab users extensively.

4.2.3 Environmental Scientist III, IV,V

- Is responsible for the technical quality of work performed.
- Communicates any technical or quality issues to the Laboratory Supervisor
- Quality Assurance Officer or Technical Director of an analytical center.
- Completes required Demonstration of Ability protocols for all procedures/methods prior to undertaking independent analysis.
- Remains current on equipment and methods used in the analysis of samples within their analytical center.
- Provides recommendations on equipment and technology needed to efficiently operate and maintain uninterrupted operation of his/her analytical duties
- Is capable of resolving technical problems encountered in the analysis of samples.
- Responsible for ordering all consumables needed for methods performed and assuring they meet standards.
- Responsible for equipment maintenance and maintenance contract oversight and acts as a liaison with service engineers to troubleshoot equipment problems.
- Generates and maintains current Standard Operating Procedures (SOPs) for Laboratory operation within his/her work that include the referenced method requirements. Assures that all SOPs are appropriately detailed for personnel performing a method or step of a method and SOP protocol is followed.
- Maintains quality assurance documentation on procedures, equipment, reagents and standards. Initiates corrective action when quality assurance data does not meet pre-established control and warning limits.
- Participates in Interlaboratory Performance Evaluation studies.
- Assures that all data generated is properly reviewed and that all reviewed data meets internal acceptance criteria or is properly flagged.
- Responsible for the generation of data packages that contain all relevant

information needed to reproduce a result and for the maintenance of both paper and electronic copies (when applicable) of data for methods performed.

- Reviews Laboratory Quality Assurance Plan revisions and follows protocols and procedures outlined within the Plan.
- Reviews data packages generated by other chemists for completeness and verifies that required quality control samples were analyzed and met acceptance criteria. Assures that primary analyst has qualified or reanalyzed samples, when established criteria are not met. Validates data in LIMS if criteria are met.

4.2.4 Environmental Assistant

- Works under the supervision of a permanent staff scientist, but is responsible for the quality of data generated.
- Follow SOPs and QA/QC requirements of methods and the Laboratory. (Procedures or steps of procedures performed by Laboratory technicians are detailed and include basic steps and precautions that may not be included in SOPs followed by environmental scientists.)
- Informs his/her immediate supervisor when precision and accuracy values are beyond established warning and control limits or other irregularities are encountered.
- Maintains QA/QC records for tests performed.
- Assists in data review for his/her analytical area.
- Is responsible for providing clean glassware and sample containers.
- Prepares bottle orders.
- Monitors the temperatures of refrigeration units, calibrates analytical balances and monitors indicator lights on the Laboratory water system on a daily basis.
- Prepares containers and other sampling items needed by samplers.
- Monitors samples dropped off and puts in appropriate storage location, may filter and/or digest samples as needed when they arrive.

4.3 Special Duties

4.3.1 Safety Officer

- Maintains and implements a Laboratory Safety Plan and Material Safety Data Sheets.
- Orients all new Laboratory employees and users to Laboratory Safety Plan.
- Monitors and maintains or oversees the maintenance of safety systems within the building.
- Responsible for the management of hazardous waste storage and disposal.

4.3.2 Quality Assurance Officer

- Reviews TNI Quality System Standard revisions and revises Laboratory Quality Assurance Policies to ensure compliance. Informs Laboratory Supervisor when in-house practices do not meet TNI standards.
- Oversees the quality control activities of the Laboratory. Advises and trains staff

in matters of QA/QC.

- Conducts annual bench audits for each analytical center which will include the Laboratory Supervisor, QA Officer and analysts within the analytical center. The audit will include but not be limited to recent PE results, irregularity report status and follow-up, adherence to DQOs listed in SOPs and addressing deficiencies listed in lab audits.
- Coordinates the scheduling, ordering, reporting and tracking of performance audits. Initiates corrective action when necessary.
- Reviews QC data and oversees development of QC data tracking and establishment of control and warning limits.
- Responsible for coordinating TNI, EPA, and NATTS audits, including implementing certification requirements, coordinating proficiency studies to maintain certification, and responding to all requests for information.
- Assures that method detection limits (MDL) are calculated on a routine basis and maintains a file of MDL data.
- Maintains an inventory of QC reference samples and materials.
- Oversees the annual instrument preventative maintenance service.
- Annually reviews and updates the Laboratory Quality Assurance Plan.
- Conducts a Laboratory Quality Assurance Program orientation for new and seasonal employees.
- Oversees the documentation, archiving and distribution of Laboratory Standard Operating Procedures (SOP). Reviews procedures for completeness. Generates SOPs for non-analytical quality related operations. .
- Ensures that staff have demonstrated initial and ongoing proficiency in the activities they are performing. Maintains training files and Initial Demonstration of Ability files.
- Verifies and maintains records on the accuracy and precision of automatic pipetting devices on a quarterly basis. Maintains records and verifies the accuracy of Laboratory thermometers.
- Assists in analytical centers when needed.
- Initiates Irregularity Reports when PE results or laboratory data are not within expected range. Assures reports are completed and reviewed in a timely fashion and staff recommended corrective actions are reasonable and likely to address the identified deficiency. Maintains a file of historic reports.

4.3.3 LIMS Administrator

- Oversees the day to day operation of the LIMS.
- Coordinate with LIMS vendor when system is not performing to lab expectations.
- Coordinates with State contracted LIMS support vendor to assure contracted work plan assignments are completed.
- Applies vendor supplied revisions and validates system after patches are applied.
- Creates and maintains parsers to allow electronic transfer of data from instruments to the LIMS.
- Trouble shoots all aspects of the LIMS.
- Creates reports and forms generated by LIMS.
- Modifies LIMS to meet TNI requirements and staff and client needs.
- Creates and maintains electronic spreadsheets that perform data transformation,

document standard and reagent traceability, calculates and tracks MDL data and captures data from Laboratory instruments.

- Maintains electronic standard/reagent electronic inventory program.

4.3.4 Technical Director

- Responsible for communicating equipment and technical support needs to the Laboratory Supervisor and assisting in the hiring of seasonal help.
- Is responsible for the technical quality of all work performed in assigned analytical center. Supervises all personnel assigned to that analytical center.
- Assures that cross-training is performed according to laboratory protocol and that properly trained staff are assigned to the analysis of samples having short hold times when necessary.
- Remains current on equipment and methods used in the analysis of samples within their analytical center. Is capable of providing insight into equipment purchases and analytical methods.
- Is capable of resolving technical problems encountered in the analysis of samples.
- Assures that routine preventative maintenance is performed on equipment in their analytical center.
- Generates and maintains current Standard Operating Procedures (SOPs) for Laboratory operation within his/her work area. Assures that all method requirements are part of the SOP and written SOPs are appropriately detailed for personnel performing the method and/or step of a method. Assures that the Lab is referencing the most current revision of a referenced method.
- Assures that the required Demonstration of Ability protocols are completed and documented for all analysts/technicians assigned to the analytical center.
- Maintains quality assurance documentation on procedures, equipment, reagents and standards. Initiates corrective action when quality assurance data does not meet pre-established control and warning limits.
- Participates in the Interlaboratory Performance Evaluation Studies.
- Assures that all data is properly reviewed and validated. May require reanalysis of samples if data quality objectives are not met prior to submitting data for approval and release.
- Reviews Laboratory Quality Assurance Plan revisions and follows protocols and procedures outlined within the Plan.
- Assures that all computer files are backed-up on a routine basis and electronic back-ups are properly documented and stored. Assures that instrument hard drives are sufficient for instrument needs and that data is removed if nearing capacity.

4.4 Laboratory Personnel

Present Specialty	Name	Position Title	Education Level: Degree & Major	Years of Experience in Current Position
Laboratory Director	T. Guy Roberts	Laboratory Director	Ph.D. Parasitology	<1
Laboratory Supervisor	Dan Needham	Environmental Scientist VI	B.A. Environmental Science	2
Laboratory Administrative Services	Alison Farnsworth	Environmental Technician III	High School Diploma 30 hours towards Business Management degree	25
Laboratory QA Officer	Dan Needham	Environmental Scientist VI	B.A. Environmental Science	1
Laboratory Safety Officer	Dan Needham	Environmental Scientist VII	B.A. Environmental Science	5
Organic Chemistry HPLC, GC, GC/MS	**VACANT**			
Organic Chemistry GC, HPLC, GC/MS	Dan Nielsen	Environmental Scientist V	Ph.D. Chemistry	4
Metals Hg Cold Vapor Analysis, ICP/MS, ICP	Anne Charbonneau	Environmental Scientist V (Technical Director Metals Lab)	B.S. Biochemistry	25
Inorganic Chemistry IC, Automated Wet Chemistry, LIMS Administrator	Dan McAvinney	Environmental Scientist IV (Technical Director Inorganic Lab)	B.S. Environmental Science	27
Metals, Wet Chemistry	Megan Phillips	Environmental Scientist I	B.A. Biology	1 ½
Microbiology	Dan Needham	Environmental Scientist VII	B.A. Environmental Science	9
Laboratory Technician	Seasonal	Environmental Tech I		

Figure 4.1 Agency of Natural Resources Organizational Chart for the Dept. of Environmental Conservation

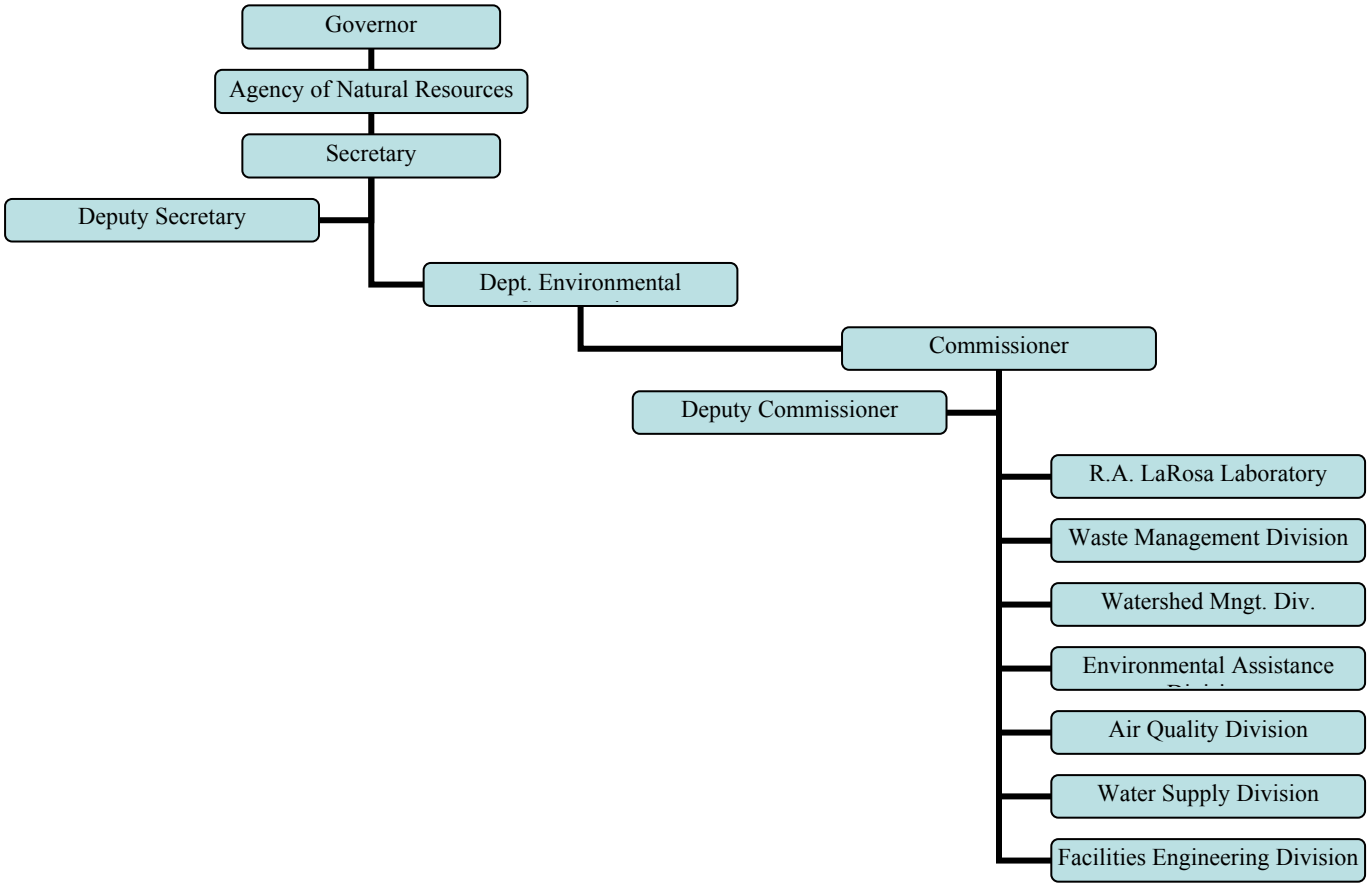
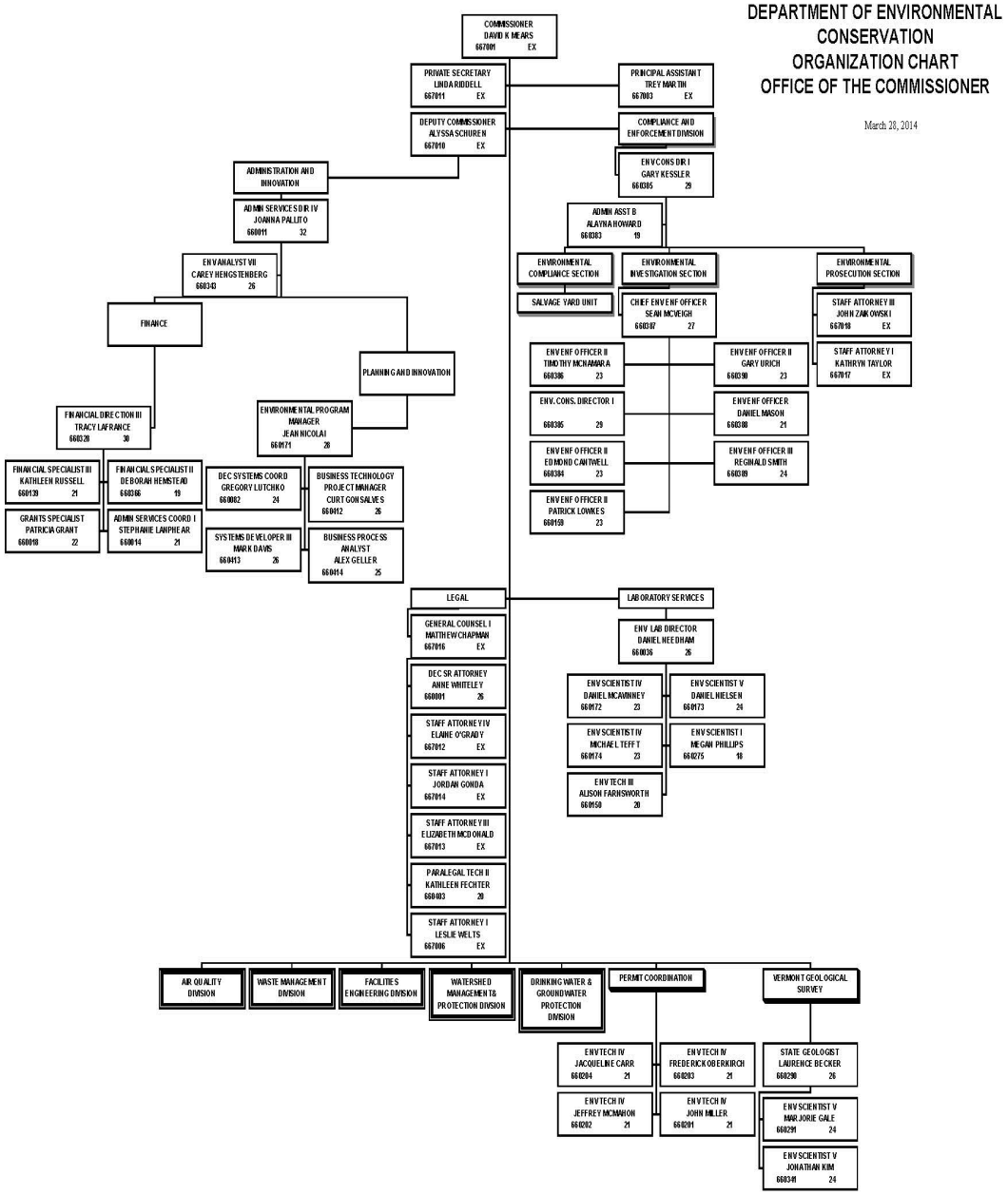


Figure 4.2 Department of Environmental Conservation Laboratory Organizational Chart



5.0 Quality Assurance Objectives

Analytical precision and accuracy are assessed through the analysis of reference standards and laboratory generated quality control samples such as analytical duplicates, matrix and surrogate spikes, and matrix spike duplicate samples. The accuracy and precision of data are related to the procedures and equipment used to analyze samples and generate data, the sample matrix being analyzed and the sample concentration. Laboratory precision and accuracy are monitored on a daily basis.

If quality assurance acceptance limits for Laboratory data are method or TNI specified the stricter criteria must be adopted. When a method does not specify limits they are established using historical Laboratory data as a guideline. Solid Waste Methods (SW-846) acceptance criteria are considered guidance, EPA Method criteria are not guidance and must be met . When insufficient data is available, default limits are used.

Laboratory quality assurance objectives for analytical data in terms of reporting limits (practical quantitation limits) and precision and accuracy, are listed by compound, method and matrix in Tables 5.1 through 5.6. Section 14 describes how data quality indicators are calculated. Precision and Accuracy objectives listed are internal or method specified limits. If internal criteria are used the limits must be narrower than method specified criteria. Sample quality control data and/or sample results are flagged when criteria are not met. If a method does not specify acceptance limits, a default objective is listed.

The lower reporting limit for a method is listed as the Practical Quantitation Limit (PQL). The low level calibration standard for a method must be at the PQL. For some methods it is recommended that the low standard is at a concentration less than the reporting limit. If accuracy is a problem at the calculated PQL due to background levels of contamination, sample dilution or other issues, the PQL will increase. If results are reported outside the calibration range they must be qualified.

Quality assurance objectives for specific projects may exceed the capabilities of the analytical methods being used. When developing project plans, project managers should specify quality assurance objectives and compare these objectives to Laboratory quality control data for the parameters of interest. When project quality assurance objectives exceed the present capabilities of the Laboratory or when an unusual matrix will be analyzed, project managers must coordinate with Laboratory management to discuss the feasibility of the project objectives. If a project requires a lower reporting limit than listed in Tables 5.1 through 5.6, the project manager should contact the Laboratory to determine if a lower limit can be achieved.

Occasionally field data is reported when a laboratory standard(s) or policy has not been met. For example, the accompanying quality control data are not within established quality objectives, sample hold times have been exceeded, Laboratory clients request data be reported below the Laboratory's established reporting limits or for some other reason the data is not to standard. Sample remark codes are used to alert the data end user to the fact that analytical data accompanied by a remark code may not be appropriate for the intended use. Final reports may also have a parameter comment that is added by the analyst to qualify a result when the data management codes do not suffice or additional qualification is needed. Final reports may also

have an order comment. An order comment will provide details on an irregularity that effects more than one sample/parameter within the order. The order comment will also be used to document any discussions the Laboratory Supervisor has had with the client regarding the analysis or disposal of non-conforming samples.

Sample Remark Codes *

Remark Code	Description
B	Reported value is associated with a lab blank contamination.
BH	Reported value may be biased high.
BL	Reported value may be biased low.
E	Estimated Value
D	Dilution resulted in instrument concentration below PQL.
H	Hold time exceeded.
I	Matrix Interference
O	Outside calibration range, estimated value.
OL	Outside Limit
P	Preservation of sample inappropriate, value may be in error.
S	Surrogate recovery outside acceptance limits.
T	Time not provided
W	Sample warm on arrival, no evidence cooling has begun.

* Codes may also be used to qualify quality control data.

"B: Reported value is associated with a lab blank contamination" is used to flag sample results when a method or continuing calibration blank criteria is not met. Associated sample results that are within a pre-specified concentration range of the associated blank data are flagged.

"BH: The reported value may be biased high" is used if the analyst determines or suspects that a sample or method bias has elevated the reported values. All samples of the same matrix may be flagged in an order comment if a representative sample shows a matrix effect.

"BL: The reported value may be biased low" is used if the analyst determines or suspects that a sample or method bias has suppressed the reported values. All samples of the same matrix may be flagged in an order comment if a representative sample shows a matrix effect.

"D: Dilution resulted in instrument concentration below PQL" is to be used when dilution is necessary to eliminate an interference for the parameter being reported. The interference can be a chemical or physical interference. For multi-parameter methods analysis and reporting from more than one dilution may be required if the interference is only compromising a portion of the chromatography. The Laboratory PQL is raised by a dilution factor.

"E: Estimated Value" The code is used under various circumstances with a Sample or Order comment explaining the irregularity. The code is also used when initial calibration or calibration

verification criteria for a parameter in a multi-parameter method have not been met. The code is only to be used under the restrictions documented in Standard Operating Procedures and will not be used in place of "O – outside calibration range, estimated value."

"H: Hold Time is exceeded" is used to flag a result when sample or extraction method specified holding times are exceeded.

"I: Matrix Interference" is used if Laboratory data quality objectives can not be met due to a matrix interference and the analyst can not determine if the bias is high or low.

"O: Outside calibration range, estimated value" is to be used for reported results that are above or below the calibration standards. It is not used if a sample dilution is made and the diluted sample result is within the calibration range. Laboratory policy requires that sample results be bracketed by standards. If there is an agreement in place with a specific Program to report below the Lab PQL, each result may not be flagged, but the report will have another form of qualification. If there is insufficient sample volume or for some other reason the sample can not be diluted and reanalyzed to bring a result(s) within calibration range the result must be flagged. If the linear dynamic range (LDR) for a method has been established and verified at the prescribed frequency, results may be reported within the LDR

"OL: Outside Limit" is used to flag data that is outside the precision or accuracy criteria established by the Lab, or referenced method.

"P: Preservation of sample inappropriate, value may be in error" is to be used when there is a decision made by the Lab to analyze an inappropriately preserved sample rather than reject the sample. The Laboratory Supervisor should be consulted and the client notified prior to proceeding with sample analysis.

"S: Surrogate Recovery outside acceptance limits" is used to flag surrogate recoveries that are outside laboratory acceptance criteria.

"T: Time not provided" Analysis with a hold time of $\leq$72 hours must have the sampling time entered at log-in and the analysis time entered by the analyst. The LIMS calculates the hold time using collection time/date and analysis time/date. If the analysis time is not entered a "T" will appear next to the analysis date and the result may not be flagged as over hold time or flagged as over hold time in error. Analysis time is required and the final report must be amended if "T" appears. If the sampling time is not entered into the LIMS at sample log-in a note will appear with the laboratory ID information on the final report and a result with a hold time of $\leq$ 72 hours may not be properly flagged.

"W: Sample warm on arrival, no evidence that cooling has begun" is to be used when samples requiring cooling arrive and are not on ice.

Table 5.1 Analytical Procedures, Practical Quantitation Levels and Corresponding Quality Assurance Objectives for Precision and Accuracy.

Parameter	Sample Type	Method Number	Ref.	PQL[a]	Units	Preci-sion[b]	Accuracy[c] % Recovery
Metals							
Aluminum	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Water	6020C, 3020A*	1	50	µg/l	20	75-125
	Water	6020A	1	10	µg/l	7.5	80-120
Antimony	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Solid	6010C, 3050B*	1	1	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	10	µg/l	7.5	80-120
Arsenic	Air	IO3.5, IO3.1*	6	1	µg/l	20	75-125
	Leachable	6020A, 1311*	1	1	mg/l		
	Solid	6010C, 3050B*	1	1	mg/kg dw	20	70-130
	Water	6020A,3020A*	1	1	µg/l	7.5	80-120
Barium	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Leachable	6020A*	1	1	mg/l		
	Solid	6010C, 3050B*	1	0.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	5	µg/l	7.5	80-120
Beryllium	Air	IO3.5, IO3.1*	6	2	µg/l	20	75-125
	Solid	6010C, 3050B*	1	0.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	1	µg/l	7.5	80-120
Cadmium	Air	IO3.5, IO3.1*	6	2	µg/l	20	75-125
	Leachable	6020A, 1311*	1	0.1	mg/l		
	Solid	6010C, 3050B*	1	0.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	1	µg/l	7.5	80-120
Calcium	Water	6010C, 3020A*	1	0.25	mg/l	20	75-125
	Water	6020A, 3020A	1	.05	mg/l	5	80-120
Chromium	Air	IO3.5, IO3.1*	6	10	µg/l	20	75-125
	Leachable	6020A, 1311*	1	2	mg/l		
	Solid	6010C, 3050B*	1	2.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	5	µg/l	7.5	80-120
Cobalt	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Solid	6010C, 3050B*	1	0.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	1	µg/l	7.5	80-120
Copper	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Solid	6010C, 3050B*	1	5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	10	µg/l	7.5	80-120
Hardness	Water	2340B	3	0.17 (ICPMS) 1.65(ICP)	mg $CaCO_3$/l		
Iron	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Solid	6010C, 3050B*	1	25	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	50	µg/l	7.5	80-120
Lead	Air	IO3.5, IO3.1*	6	1	µg/l	20	75-125
	Leachable	6020A, 1311*	1	1	mg/l		
	Solid	6010C, 3050B*	1	0.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	1	µg/l	7.5	80-120
Magnesium	Solid	6010C, 3050B*	1	1	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	0.25	mg/l	20	75-125
	Water	6020A	1	.01	mg/l	5	80-120
Manganese	Air	IO3.5, IO3.1*	6	1	µg/l	20	75-125
	Solid	6010C, 3050B*	1	5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	5	µg/l	7.5	80-120
Mercury	Fish	7471B, 3051A*	4,1	0.05	mg/kg ww	20	70-130
	Leachable	7471B, 1311*	4,1	0.05	mg/l	20	80-120
	Solid	7471B	1	0.04	mg/kg dw	20	80-120

Parameter	Sample Type	Method Number	Ref.	PQL[a]	Units	Preci-sion[b]	Accuracy[c] % Recovery
	Water	245.1	4	0.2	µg/l	5	85-115
Molybdenum	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Solid	6010C, 3050B*	1	0.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	5	µg/l	7.5	80-120
Nickel	Air	IO3.5, IO3.1*	6	10	µg/l	20	75-125
	Leachable	6020A, 1311*	1	3	mg/l		
	Solid	6010C, 3050B*	1	0.5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	5	µg/l	7.5	80-120
Potassium	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Water	6010C, 3020A*	1	.50	mg/l	20	75-125
	Water	6020A	1	.05	mg/l	5	80-120
Selenium	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Leachable	6020A, 1311*	1	1	mg/l		
	Solid	6010C, 3050B*	1	2.5	mg/kg dw	20	70-130
	Water	6020A,3020A	1	5	µg/l	7.5	80-120
Silver	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Leachable	6020A, 1311*	1	1	mg/l		
	Solid	6010C, 3050B*	1	1	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	1	µg/l	7.5	80-120
Sodium	Water	6010C, 3020A*	1	0.25	mg/l	20	75-125
	Water	6020A	1	.05	mg/l	5	80-120
Strontium	Solid	6010C, 3050B*	1	1	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	10	µg/l	7.5	80-120
Thallium	Solid	6010C, 3050B*	1	5	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	1	µg/l	7.5	80-120
Uranium	Solid	6020A, 3050B*	1	0.1	mg/kg dw	20	70-130
	Water	6020A, 3020A*	1	1	µg/l	7.5	80-120
Vanadium	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Solid	6010C, 3050B*	1	5	mg/kg dw	20	70-130
	Water	6020A,3020A	1	25	µg/l	7.5	80-120
Zinc	Air	IO3.5, IO3.1*	6		µg/l	20	75-125
	Leachable	6020A, 1311*	1	50	mg/l		
	Solid	6010C, 3050B*	1	1	mg/kg dw	20	70-130
	Water	6020A,3020A	1	50	µg/l	7.5	80-120
Microbiology							
Coliform – Total Colilert	Water	9223B	3	1	MPN/100mls	125 (≤25 mpn) 75 (>25 mpn)	
Coliform, E. coli – Colilert	Water	9223B	3	1	MPN/100ml	125 (≤ 25 mpn) 75 (> 25 mpn)	
Inorganic Chemistry							
Alkalinity	Water	2320B	3	1	mg $CaCO_3$/l	5 (>20mg/l) 15 (<20mg/l)	
BOD Uninhibited 5-Day	Water	5210B	3	1	mg/l	35	80-120
Chlorine, Total	Water	8167	8	0.02	mg/l	10	80-120
Chloride	Water	4500-Cl^- G.	3	2	mg/l	5	85-110
Chloride-Ion Chrom.	Water	300.0	2	0.2	mg/l	5	90-110
Chlorophyll-a	Water	445.0	7	0.5	µg/l	10	
Chemical Oxygen Demand (COD)	Water	Hach 8000	8	15	mg/l	25	75-125
Conductivity	Water	2510B	3	1	umhos/cm	5	
Fluoride	Water	300.0	2	0.5	mg/l	5	90-110
Nitrogen, Ammonia	Water	4500-NH_3 H (see footnote i)	3	0.05	mg-N/L	5	80-120
Nitrogen, Nitrate-Ion Chrom	Water	300.0	2	0.02	mg-N/L	5	90-110

Parameter	Sample Type	Method Number	Ref.	PQL[a]	Units	Preci-sion[b]	Accuracy[c] % Recovery
Nitrogen, Nitrate/Nitrite	Water	4500-NO_3^- I.	3	0.05	mg-N/L	5	85-110
Nitrogen, Nitrite-Ion Chrom.	Water	300.0	2	0.1	mg-N/L	10	85-115
Nitrogen, Total Kjeldahl	Water	4500-Norg D	3	1	mg-N/L	20	75-125
Nitrogen, Total Persulfate	Water	4500-N C-modified	3	0.1	mg-N/L	10	85-115
Oxygen, Dissolved	Water	4500-O C.	3	.05	mg/l	8	
pH	Water	4500-H+B	3		Std. Unit	5	
	Soil	9045C	1		Std. Unit		
Phosphorus-Ortho	Water	4500-P H.	3	5	µg/l	15	
Phosphorus-Dissolved	Water	4500-P H.	3	5	µg/l	15	85-115
Phosphorus-Total	Water	4500-P H.	3	5	µg/l	15	85-115
Silica, (SiO_2) Dissolved	Water	4500-SiO_2 F.	3	0.2	mg/l as SiO_2	5	85-115
Solids,Total Volatile	Solid	2540-G	3		percent	5 j	
	Water	2540-E	3		mg/l	5	
Solids, Percent	Solid	2540-G	3		percent	5 j	
Solids, Total Dissolved	Water	2540-C	3	5	mg/l	5	80-120
Solids, Total Suspended	Water	2540-D	3	1	mg/l	15k	
Sulfate – Ion Chrom	Water	300.0	2	0.5	mg/l	5	90-110
Turbidity	Water	2130B	3	0.2	NTU	15	
Organics (See Cover page note)							
Carbonyl Compounds	Air	TO-11A	5	g	µg/cartridge	10	e
Total Petroleum Hydrocarbons - Diesel Range Organics (DRO)	Solid	8015B modified:3510C*	1	200	mg/kg dw	25	e
	Water	8015B modified: 3510C*	1	0.2	mg/l	25	e
Volatile Organics	Solid	8260C, 5035A*	1	d	µg/kg dw	25	e
	Water	8260C, 5030C*	1	d	µg/l	25	e
Volatile Organics – Aromatics	Water	8021B	1	f	µg/l	25	e
	Solid	8015, modified	1	10	mg/kg dw		
Volatile Organics – Gasoline Range Organics (GRO)	Water	8015B, modified	1	200	µg/l		
Volatile Organics	Air	TO-15	5	h	ppb v	25	e

References:

1. Test Methods for Evaluating Solid Wastes, (SW846).

2. Methods for the Determination of Inorganic Substances in Environmental Samples; EPA/600/R-93/100.

3. Standard Methods for the Examination of Water and Wastewater; 21st Ed. 2005.

4. Methods for the Determination of Metals in Environmental Samples – Supplement 1; EPA/600/R-94/111.

5. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air; EPA/625/R-96/010B. 2nd Edition. January 1999.

6. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air; EPA/625/R-96/010a. June 1999.

7. In vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence, Method 445.0, Revision 1.2, September 1997. National Exposure Research Laboratory Office of Research and Development. U.S. Environmental Protection Agency.

8. Hach Handbook of Water Analysis, 1979. Hach Chemical Company.

Footnotes:

* Sample Preparation Method

a Practical Quantitation Limits (PQL) is the lower limit of quantitation (reporting). Lower reporting limits may be achievable. Contact Laboratory for project specific requests.

b Laboratory Analytical Duplicate Relative Percent Difference (RPD) acceptance criteria. RPDs will be less for most duplicate values but higher for results near the PQL. Limits are method specified or generated from historical Laboratory data.

c Sample Matrix Spike Analyte Percent Recovery acceptance criteria are method specified limits or generated from historical Laboratory data. Recoveries are matrix/sample dependent

d PQLs are listed in Table 5.2.

e Precision and Accuracy acceptance limits can be found in referenced method or Laboratory Standard Operating Procedures.

f PQLs are listed in Table 5.3

g PQLs are listed in Table 5.4

h PQLs are listed in Table 5.5

i Preliminary distillation is not performed. Laboratory does not accept NPDES ammonia samples requiring distillation.

j Duplicate Relative Percent Differences (RPDs) for samples with low percent solids or non-homogeneous samples (i.e. rocks and light sediment) will be higher than the value listed.

k Precision and Accuracy for samples high in heavy sediment may be outside listed criteria. The entire sample volume can not be filtered and heavy particles settle quickly while decanting an aliquot of sample.

Table 5.2 Method 8260 Practical Quantitation Limits (PQLs) for Water and Soil.

Parameters Measured	Practical Quantitative Limits	
	Water[a] ug/l	**Soil[b] µg/kg dw**
Acetone	25	6250
Benzene	1	125
Bromodichloromethane	1	125
Bromoform	2	250
Bromomethane	5	125
2-Butanone (MEK)	25	6250
Carbon disulfide	2	125
Carbon tetrachloride	2	250
Chlorobenzene	2	250
Chloroethane	2	250
Chloroform	1	125
Chloromethane (methylchloride)	2	250
Dibromochloromethane	2	250
Dichlorodifluoromethane	5	125
1,1-Dichloroethane	1	125
1,2-Dichloroethane	2	250
1,1-Dichloroethene	1	125
cis-1,2-Dichloroethene	1	125
trans-1,2-Dichloroethene	1	125
1,2-Dichloropropane	2	250
cis-1,3-Dichloropropene	1	125
trans-1,3-Dichloropropene	1	125
Ethylbenzene	1	125
2-Hexanone	25	6250
Methylene chloride	5	625
Methyl-t-Butylether (MTBE)	1	125
4-Methyl-2-pentanone(MIBK)	25	6250
Styrene	2	250
1,1,2,2-Tetrachloroethane	1	125
2-Chlorotoluene	2	250
Tetrachloroethene	1	125
Tetrahydrofuran	25	6250
Toluene	1	125
1,1,1-Trichloroethane	1	125
1,1,2-Trichloroethane	1	125
Trichloroethene	1	125
Trichlorofluoromethane	1	125
Vinyl acetate	10	1250
Vinyl chloride	2	250
m+p – Xylenes	2	250
o-Xylene	1	125
Naphthalene	2	250
1,2,4-Trimethylbenzene	1	125
1,3,5-Trimethylbenzene	1	125
1,4-Dichlorobenzene	2	250
4-Isopropyltoluene	2	250

[a] PQL for water is a judgmental evaluation based on calculated MDL, instrument response factors and method interference.

[b] PQL for soils/sediment are for the high concentration technique described in Method 5035.

Table 5.3 Method 8021 Practical Quantitation Limits (PQLs)

Parameter	Water µg/l
Benzene	1
Ethylbenzene	1
Toluene	1
p + m Xylenes	2
o-Xylenes	1
MTBE	1
1,3,5-Trimethylbenzene	1
1,2,4-Trimethylbenzene	1
Naphthalene	2

Table 5.4 Method TO11 Practical Quantitation Level (PQL)

Parameter	PQL µg/cart[a]
Formaldehyde	.05
Acetaldehyde	.05
Acetone	.05
Propionaldehyde	.05

[a] The PQL listed is the concentration of low standard. The low standard is .01 µg/ml which equals .05 µg/cartridge. Results reported below this value, are flagged.

Table 5.5 Method TO15 Target Compounds and Practical Quantitation Limits (PQLs)[a]

Target Compounds	PQLs (Low Standard ppbv)[a]
Acetylene[b]	.10
Propene[c]	.10
Dichlorodifluoromethane (freon-12)	.10
Chloromethane	.10
1,2-Dichlorotetrafluoroethane (freon-114)	.10
Vinyl Chloride	.10
1,3-Butadiene	.10
Bromomethane	.10
Chloroethane	.10
Trichlorofluoromethane (freon-11)	.10
Acrolein	.10
Acrylonitrile	.10
1,1-Dichloroethene	.10
Methylene Chloride	.10
3-Chloropropene	.10
1,1,2-Trichlorotrifluoroethane (freon-113)	.10
Trans-1,2-Dichloroethene	.10
1,1-Dichloroethane	.10
Methyl tert-Butyl Ether	.10
Methyl Ethyl Ketone	.10
Cis-1,2-Dichloroethene	.10
2-Chloro-1,3-Butadiene	.10
Bromochloromethane	.10
Chloroform	.10
Ethyl tert-Butyl Ether	.10
1,2-Dichloroethane	.10
1,1,1-Trichloroethane	.10
Benzene	.10
Carbon Tetrachloride	.10
tert-Amyl Methyl Ether	.10
1,2-Dichloropropane	.10
Ethyl Acrylate	.10
Trichloroethene	.10
Bromodichloromethane	.10
Methyl Methacrylate	.10
Cis-1,3-Dichloropropene	.10
Methyl Isobutyl Ketone	.10
Trans-1,3-Dichloropropene	.10
1,1,2-Trichloroethane	.10
Toluene	.10

Target Compounds	PQLs (Low Standard ppbv)[a]
Dibromochloromethane	.10
1,2-dibromoethane	.10
n-Octane	.10
Tetrachloroethene	.10
Chlorobenzene	.10
Ethylbenzene	.10
p & m-xylene	.10
Bromoform	.10
Styrene	.10
o-xylene	.10
1,1,2,2-Tetrachloroethane	.10
1,3,5-Trimethylbenzene	.10
1,2,4-Trimethylbenzene	.10
1,3-Dichlorobenzene	.10
*Benzyl Chloride	.10
1,4-Dichlorobenzene	.10
1,2-Dichlorobenzene	.10
1,2,4-Trichlorobenzene	.10
Hexachloro-1,3-Butadiene	.10

* not guaranteed by Linde Electronic and Specialty Gas.

a Values below the lowest curve value (0.10 ppbv) are reported as per client request.

b Acetylene not separated from ethane and ethene.

c Propene not separated from propane.

6.0 Sample Handling

6.1 Sample Collection

Agency personnel, Agency contracted site investigators or volunteer monitors are responsible for collecting and delivering samples to the DEC Laboratory. The Laboratory does not accept samples collected by the general public. Agency personnel are responsible for developing Standard Operating Procedures (SOPs) that describe the fieldwork they perform and insuring that hired contractors and volunteer monitors are trained in the collection and handling of samples. Table 6.1 describes the required containers, preservation and holding times for the parameters analyzed at the Laboratory. Sample collection and handling protocols are available for:

- Microbiology Samples
- Volatile Organic Soil and Volatile Organic Water
- Phosphorus
- Dissolved Oxygen

6.2 Sample Receiving

Most samples are delivered, logged into the Laboratory Management System, labeled, preserved, subdivided, filtered if necessary and stored in refrigeration units by Agency staff or volunteer monitors responsible for the collection of the sample(s). Sample temperature upon delivery is monitored and the temperature of a representative sample is recorded in the LIMS by Agency staff. A sample preparation room is dedicated to the processing and storage of samples received at the Laboratory. Dedicated refrigeration units are used for samples that could become contaminated. Sample log in instruction and chain of custody sample handling instructions are described in Section 7.0.

A limited number of samples arrive by courier. Sample Login sheets are submitted with samples that are mailed to the lab or are submitted by volunteers, non-agency personnel or Agency personnel that request that Lab staff log-in their samples. The Sample Log-In Sheet is used by field personnel to record required information (Figure 6.1). The Laboratory secretary, supervisor or analyst records required information at check in, such as preservation, temperature, date and time received and laboratory initials who received samples. Samples information is entered into LIMS and labeled accordingly.

Chemical preservation of samples is performed by laboratory or field staff. A Sample Log-in Report is generated at the time the samples are entered into the LIMS. If an analysis requires preservation, it is documented at the time of sample preparation.

6.3 Sample Preservation

6.3.1 Temperature Preservation

Samples requiring thermal preservation will be considered acceptable if there is evidence that the chilling process has begun, such as arrival on ice for samples that are delivered to the Laboratory the day of collection.

If samples require thermal preservation and they are not delivered on the day of collection they will be considered acceptable if the arrival temperature is either within 2°C of the required temperature or the method specified range. For example if the specified temperature is 4°C, sample temperature ranging from above freezing to 6°C is acceptable.
When samples are received at the laboratory, date, time, temperature and receiving person's initials are recorded on paperwork and in LIMS.

6.3.2 Chemical Preservation

In most instances chemical preservation can be initiated upon delivery of samples to the Laboratory if samples are delivered the day of collection. If field preservation is required the sample container provided will contain the required preservative.
If samples have not been field preserved Agency employees or lab staff must preserve the samples at the Lab following protocols outlined in Table 6.1 *Summary Chart: Required Containers, Preservation and Holding Times.*
All samples requiring acid preservation must be tested for proper pH prior to or after analysis. Preservation is verified by the analysts and documented on bench sheets or in laboratory notebooks. If a sample(s) was not properly preserved and if the sample has not
already been analyzed prior to pH verification, the client may be notified before proceeding with analysis if practical (metals samples are an exception, policy is to preserve and wait 16 hours to analyze). If the sample was not properly preserved and the client requests that sample results be released the analyst must flag data with a "P- preservation of sample inappropriate, value may be in error". The Laboratory Supervisor must document in writing the clients decision to report results that do not meet acceptance criteria. The documentation is usually done in the LIMS "Order Comment" field which is displayed on the first page of a client's Final Report.

6.4 Sample Acceptance and Rejection Policy

6.4.1 Sample Acceptance

6.4.1.1 Required Information:

Samples submitted to the Laboratory must be accompanied with the following information either electronically by means of typing the information into the Laboratory Information System (LIMS) at sample log-in time or by completing a

Sample Log-In Sheet if samples are to be logged in by Laboratory staff:

- Customer Identification and Contact
- Identification of Individual Logging in Sample (documented in "Comment for Entire Order" field
- Date of Collection
- Time of Collection (time must be entered for all tests with a holding time of $\leq$ 72 hours)
- Collector's Name
- Activity Code (if applicable for billing by activity)
- Preservation Y/N
- Sample Matrix (solid, water, air, fish)
- Customer Sample Identification(s)
- Requested Tests
- Sample Remarks
- Sample Condition (Located under Edit Menu of Header)
    - Have samples arrived on ice? Yes/No
    - Temperature of representative sample (^{o}C)

Individuals submitting samples requiring "legal" Chain of Custody (COC) must follow protocol outlined in the Laboratory QA Plan: Section 7.2 Chain of Custody Procedures. A DEC Lab COC Form must be submitted with the samples. If protocols are not followed the laboratory supervisor or his designated representative will refuse samples unless written instructions from the client instruct the laboratory to proceed with analysis. The final Lab Report will document irregularities and the client's decision on how the Lab was instructed to proceed i.e. discard samples or analyze and report results with a qualifier.

6.4.1.2 Sample Labeling:

Samples must be clearly labeled with a unique identification. Labels should be water resistant and indelible ink used. At sample Login the LIMS will print a label for each sample container that will contain all required information. Labels will have unique bar codes that allow analysts to enter Sample ID #s into laptop spreadsheets or analytical instrument data bases.

6.4.1.3 Sample Containers:

Samples must be collected in appropriate sample containers provided by the Laboratory. Bottle order forms identify which bottle to use for each parameter. *See Laboratory QA Plan; Table 6.1 Summary Chart: Required Containers, Preservation and Holding Time.* If the Laboratory Supervisor accepts a sample in a container not provided by the lab a Sample Note or Order Comment must be added to the LIMS.

6.4.1.4 Sample Holding Times:

Samples must be delivered to the Laboratory to allow sample analysis to be completed within sample hold time. Samplers must schedule pH and chlorine (These parameters need to be "analyzed immediately" and will always be flagged as exceeding hold time), Microbiology (8 hour hold time for Environmental samples and Source Drinking Water samples and 30 hours for drinking waters), Dissolved Oxygen (8 hour hold time), BOD5 (24 hour hold time), nitrite, nitrate, orthophosphate, and turbidity (48 hour hold time). Sample holding times for other parameters are listed in the *Laboratory QA Plan; Table 6.1 Summary Chart: Required Containers, Preservation and Holding Time.* Samples must arrive so that analysis can be completed within the hold time. Sample delivery constraints will apply to samples that need to be processed within 48 hours or less.

6.4.1.5 Sample Volume:

Appropriate sample volume must be provided. Containers, which are provided for each test, will provide the appropriate volume if filled. Instructions on filling sterile microbiology bottles, total phosphorus tubes, and volatile vials (solid and water) must be followed. An additional sample volume may be required for some tests to provide the Laboratory with the sample volume required to perform required QC. If additional volume is needed, sample bottles will be labeled with a "Collect Sample for Duplicate/Spike" label by Laboratory personnel. Samplers are instructed to collect an extra volume of sample and designate the sample as a duplicate and/or matrix spike sample. The labeled containers are not logged into the data management system but must be labeled with the sample identification number of the field duplicate sample that is logged in. It is essential that the sample is collected as a full volume and split between the two containers. This is not possible with VOA samples and extra vials are collected as individual samples.

6.4.1.6 Sample Preservation:

Sample preservation protocols outlined in Section 6.3 Sample Preservation, and Table 6.1 *Summary Chart: Required Containers, Preservation and Holding Time* must be followed.

6.4.2 Sample Rejection:

If a sample is received that is not suitable for testing or insufficient details are provided for the Laboratory to proceed the client must be consulted for further instructions before proceeding with analysis.

The Laboratory Supervisor determines if submitted samples are to be rejected or results not reported for samples that have already been processed. Laboratory staff must immediately inform the Supervisor of any non-conformities that may affect the validity of sample results. TNI requires that the Laboratory shall either:

- retain correspondence and/or records of conversations concerning the final disposition of rejected samples; or
- fully document any decision to proceed with the analysis of samples not meeting acceptance criteria.

When samples do not meet Laboratory requirements, they are either rejected or reported with a comment for the appropriate tests. In either case the program manager is contacted in writing (e-mail or letter) requesting concurrence with the Laboratory's decision to reject the samples or to proceed with the analysis. An appropriate comment must appear on the Laboratory Final Report.

If samples are accepted analysis data will be "qualified" on the final report. A sample comment or remark code must be included on the LIMS to record any sample abnormality or departure from standard condition prescribed in the relevant test method. The Lab deletes rejected samples from the LIMS in order to prevent the client from being charged for the test. An appropriate order comment should be added to the LIMS letting the clinet know why a sample was rejected and deleted form the system.

Samples may be rejected for the following reasons.

- Insufficient volume.
- Inappropriate container.
- Sample beyond hold time or Laboratory is unable to perform analysis within required hold time.
- Inappropriate sample preservation or sample chilling has not begun for samples requiring thermal preservation.

6.5 Sample Containers, Preservation and Holding Times

Appropriate containers, preservation and sampling holding times can be found in Table 6.1. Parameters are organized alphabetically by analytical centers (metals, microbiology, inorganic chemistry and organics).

Figure 6.1 Sample Log-In Sheet

Sample Log-In Sheet

Customer ID: (formerly program #)		
Collected by:	Phone #:	Date Collected: **Time Collected*:**
Submitted by:	Phone #:	Date Submitted: **Time Submitted:**
Lab Report To:	Mailing Address:	Preserved Y N
Project ID # (formerly Activity Code #):	Project ID # Description:	Samples Arrived on Ice: Y N Temperature Control* * °C
Sample Comments: (notes apply to all samples logged in with this batch unless otherwise noted – the comments **ONLY** appear on the log-in receipt – analytical staff **DO NOT see the** comments.)		

Tests Requested
(applies to each "site" unless noted otherwise)

***For VOCs, the Lab staff must be alerted if the concentration of VOC is expected to be greater than 1 ppm.**

Customer Sample ID
(include time of collection for all samples)., i.e. St. Albans - MW1 13:30

Comments to Laboratory personnel:

* If time collected is different for each sample list the times next to Customer Sample IDs.

****Temperature Control - select a representative sample from the group and use the IR thermometer to take the sample temperature. Record this temperature and also note whether the samples arrived on ice or not.**

Table 6.1 Summary Chart: Required Containers, Preservation and Holding Times

Parameter	Sample Matrix	Container	Preservation	Maximum Hold Time	Note
Metals					
Calcium, magnesium, potassium, sodium, aluminum	Water	P, 125ml round (**Acid Rain only**)	HNO_3 to pH <2	6 months	a,b
Mercury	Solid	P, 250 ml round (half full)	Cool, ≤6°C	As soon as possible but within 28 days	k
Mercury	Water	P, 250ml round	HNO_3 to pH <2	28 days	a,b
Metals	Water	P, 250ml round	HNO_3 to pH <2	6 months	a,b
Metals (TCLP – see footnote m)	Liquid Sludge	P, 1000ml or P, 2000ml (2 containers /sample) sample size depends on % solids. Consult Lab Supervisor.	Cool, ≤6°C	6 months	k
Metals (TCLP – see footnote m)	Solid	P, 250ml round (half full)	None- Freeze or ≤6°C if samples will not be analyzed within 6 months	6 months	k
Microbiology					
Coliform – Total and/or E. coli	Water	P, 290 or 120ml sterile	Cool, <10°C	6 hours	c,m,o
Inorganic Chemistry					
Alkalinity	Water	P, 250ml square	Cool, ≤6°C	14 days	
BOD Uninhibited 5-Day	Water	P, 2 L	Cool, ≤6°C	48 hours	c,f
Chloride	Water	P, 50ml centrifuge tube, purple cap	none required	28 days	i
Chloride – (Ion Chromatography)	Water	P, 50ml centrifuge tube, purple cap	Cool, ≤6°C	28 days	i
Chlorine	Water	G, 125ml amber	Cool, ≤6°C	analyze immediately	
Chlorophyll-a	Water	glass fiber filter, Whatman GF/F, 47mm, 0.7µm pore size stored in black jar	Freeze filter in black jar – 20 to -70°C	21 days	
Chemical Oxygen Demand (COD)	Water	P, 50ml centrifuge tube, blue cap	Cool, ≤6°C, H_2SO_4 to pH <2	28 days	e
Conductance	Water	P, 250ml, square	Cool, ≤6°C	28 days	
Fluoride (Ion Chromatography)	Water	P, 50ml centrifuge tube, purple cap	Cool, ≤6°C	28 days	i
Nitrogen, Ammonia	Water	P, 50ml centrifuge tube, blue cap	Cool, ≤6°C, H_2SO_4 to pH <2	28 days	e
Nitrogen, Nitrate (Ion Chromatography)	Water	P, 50ml centrifuge tube, purple cap	Cool, ≤6°C, **Do Not Acidify**	48 hours	i
Nitrogen, Nitrate+Nitrite	Water	P, 50ml centrifuge tube, blue cap	Cool, ≤6°C, H_2SO_4 to pH <2	28 days	e
Nitrogen, Nitrite	Water	P, 50ml centrifuge tube, purple cap	Cool, ≤6°C **Do Not Acidify**	48 hours	c,i
Nitrogen, Total Kjeldahl	Solid	P, 250ml round	Cool, ≤6°C	28 days	
Nitrogen, Total Kjeldahl	Water	P, 250ml round	Cool, ≤6°C, H_2SO_4 to pH <2	28 days	e
Nitrogen, Total Persulfate	Water	P, 50ml centrifuge tube, blue cap	Cool, ≤6°C, H_2SO_4 to pH <2	28 days	e
Nitrogen, Total Dissolved Persulfate	Water	P, 50ml centrifuge tube, blue cap	Cool, ≤6°C, H_2SO_4 to pH <2	28 days	a, e
Oxygen, Dissolved	Water	G, 300ml D.O. bottle	$MnSO_4$, Alkalide iodide solution. Store in dark	8 hours	c, g
pH	Water	P, 250ml	none required	analyze immediately	q

Parameter	Sample Matrix	Container	Preservation	Maximum Hold Time	Note
Phosphorus-Ortho	Water	G, 60ml vials	Filter within 15 minutes, (.45µm) Cool, ≤6°C	48 hours	c,i,n
Phosphorus, Total	Water	G, 60ml vials	none	28 days	j,n
Phosphorus, Total Dissolved	Water	G, 60ml vials	Filter immediately (0.45µm)	28 days	i,j,n
Silica	Water	P, 50ml centrifuge tube, purple cap	Filter imm. for diss. (.45µm membrane filter - **not glass fiber**) Cool, ≤6°C	28 days	
Solids -Total Dissolved	Water	P, 250ml square	Cool, ≤6°C	7 days	
Solids - Total Suspended	Water	P, 1 L	Cool, ≤6°C	7 days	
Solids - Total Volatile	Solid	P, 50ml centrifuge tube, purple cap	Cool, ≤6°C	7 days	p
Solids - Total Volatile	Water	P, 250ml square	Cool, ≤6°C	7 days	
Sulfate – (Ion Chromatography)	Water	P, 50ml centrifuge tube, purple cap	Cool, ≤6°C	28 days	i
Turbidity	Water	P, 250ml square	Cool, ≤6°C	48 hours	
Organics					
Carbonyl Compounds	Air	DNPH-cartridge	Cool, ≤6°C	14 days to extraction, 30 days after	l
Total Petroleum Hydrocarbons – 8015 (Diesel Range Organics (DRO)	Water	G, 1 L amber, Teflon lined caps (2 containers/sample if duplicate, MS or MSD is required)	Cool, ≤6°C, HCl to pH<2	7 days to extraction, 40 days after	n
Total Petroleum Hydrocarbons – 8015 Diesel Range Organics (DRO)	Solid Liquid Sludge	G, 125ml amber, Teflon lined cap G, 500ml amber, Teflon lined cap	Cool, ≤6°C	14 days to extraction, 40 days after	
Volatile Aromatics and MTBE (8021)	Water	G, two-40ml vials with Teflon lined caps/sample.	Cool, ≤6°C, HCl to pH <2	14 days	d,k,r
Volatile Organics (8260)	Water	G, three-40ml vials per sample, Teflon lined caps.	Cool, ≤6°C, HCl to pH <2	14 days	d,h,r
Volatile Organics (8260) (high concentration samples)	Solid	G, 40ml vial pre-weighed with methanol. G, 40ml vial without methanol to be used for % solid **Both samples required.**	Cool, ≤6°C	14 days	m,r
Volatile Organics	Air	Air Canister 6 L	Room Temperature	30 days	l
Volatile Organics – Gasoline Range Organics (GRO)	Water	G, two – 40ml vials per sample, Teflon lined caps/sample	Cool, ≤6°C, HCl to pH <2	14 days	h
Volatile Organics – Gasoline Range Organics (GRO)	Solid	G, 40ml vial pre-weighed with methanol. G, 40ml vial without methanol to be used for % solid **Both samples required.**	Cool, ≤6°C	14 days	m,r

G = glass
P = plastic

Notes:

a "Dissolved" analytes or turbid samples must first be filtered through 0.45µm membrane filter followed by acid preservation. A filter blank must be submitted with each batch of filtered samples.

b Add ~0.1% (v/v) concentrated nitric acid to sample volumes. Approximately 0.5ml/250 ml

c Lab needs prior notice for this parameter. Samples must be delivered to the Lab several hours prior to maximum hold time.

d Chlorinated samples need to be collected in sample bottle containing .008% sodium thiosulfate - $Na_2S_2O_3$ (.0032 g for 40 ml; 0.16 g for 2000 ml; 0.208 g for 2600 ml).

e Approximately 0.1 ml concentrated H_2SO_4/50 ml centrifuge tube (blue cap). Reagent grade, low level nitrogen (<5 ppm) sulfuric acid required for nitrogen parameters.

f Hold time is from the end of sample collection period. Maximum composite time is 24 hours.

g Samples must be "fixed" in field with 2 ml of manganese sulfate (DO #1)and then 2 ml of alkalide iodide (DO#2). Store samples in the dark and analyzed within 8 hours.

h No head space, vials preacidified with 0.4 ml 1:1 HCl. Two acidified trip blanks must be brought into the field with each sample set.

i Samplers must filter sample through 0.45 µm membrane filter. For ion chromatography a single sample container of 50 ml is sufficient for all five anions (chloride, fluoride, sulfate, nitrate and nitrite). A filter blank is required. Filter Blank is logged into the LIMS as a sample.

j Samplers must fill to the 50 ml mark (black line).

k TCLP work requires two separate samples of the listed volume. Sample size depends on % solids, a minimum of 200 g is required/sample. Sample must undergo TCLP extraction within the following time periods.

Sample Maximum Holding Times (Days)

	From: Field Collection To: TCLP Extraction	From: TCLP Extraction To: Preparative Extraction	From: Preparative Extraction To: Analysis	Total Elapsed Time
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals except mercury	180	NA	180	360

NA = not applicable

l Sample handing procedures are described in Air Toxic Monitoring Quality Assurance Project Plan.

m Sampling instructions provided by lab must be followed.

n A second volume is required in order to perform a matrix spike or a duplicate analysis.

o Chlorinated samples must be collected in sterile 120 ml sample bottles containing sodium thiosulfate - $Na_2 S_2O_3$.

p Samples are routinely frozen upon receipt and processed as soon as possible. If sample sieving is required it is performed by field staff.

q If lab analysis of pH is requested sample should be analyzed immediately. Fill container to brim. No headspace.

r If a client requires duplicate or matrix spike analysis the Laboratory must be provided with an extra vial for each request. If sample site contamination level is unknown, an extra sample vial will help insure that appropriate sample dilutions can be made.

7.0 Sample Management

7.1 Laboratory Information Management System

The Laboratory Information Management System (LIMS) consists of two parts: The front end is a Microsoft Access database and a back end which uses Microsoft SQL to store the data. A record of all samples submitted to the laboratory for analysis is logged into the LIMS. The LIMS performs the following functions:

- Sample management and tracking.
- Bar coding of samples.
- Data management, (data entry, validation, approval).
- Quality control data tracking.
- Electronic data transfer/acceptance from laboratory instruments and Excel files.
- Billing and customer information.
- Chain of custody tracking.
- Data reporting (electronic and paper).

Detailed instructions are available for individuals that are required to login samples. The system is secure and provides an audit trail for entries and changes. There are several levels of access to LIMS functions. The data base administrator allocates the appropriate level of access to each lab employee and outside users.

7.2 Legal Chain of Custody Procedures

7.2.1 Introduction

Before deciding to use legal chain of custody procedures to insure that laboratory results can be used for litigation and enforcement, the collection and analysis of samples must be part of a well-organized plan. The plan will delineate what, where and how the samples are taken and establish the level of quality assurance needed. A plan calling for chain of custody procedures will require documentation of sample integrity from collection to final disposition by the Laboratory.

Chain of Custody Procedures are necessary to insure the legal integrity of sample materials collected and submitted to the Environmental Conservation Laboratory for analysis. The validity of the test results is assured if the Department can show that after the samples were collected, they were kept safe from tampering or chemical contamination. This requires that complete written documentation of the security of the sample from collection to disposition be kept.

7.2.2 Sample Custody

A sample is under custody if:

- it is in your possession, or
- it is in your view, after being in your possession, or
- it was in your possession and then you locked it up to prevent tampering, or

- it is in a designated secure area.

7.2.3 Submittal of Samples

Any user of the DEC Laboratory can request chain of custody handling of their samples; these requests presume that the results are likely to be used for enforcement. Individuals taking samples, which require chain of custody procedures, are DEC personnel, consulting companies under contract to the Department or non-department personnel taking samples to support a Department program.

Whether samples are hand carried or delivered by a courier they must be properly preserved individually sealed and include a Chain of Custody Record. After receipt of the sample, a copy of this record is returned to the sampler. To track their samples from collection in the field to receipt of a laboratory report, DEC consultants frequently use either a generic or their own chain of custody transfer record form and do not seal the individual sample containers. This procedure will not meet the State's requirements for chain of custody samples. While DEC allows consultants to use this procedure to track their samples, without the use of seals and the DEC Chain of Custody Record this procedure does not satisfy the State's burden for demonstrating that proper chain of custody procedures were followed in the handling and processing of samples.

Hand Carried – This is the most common approach and is used almost exclusively by DEC personnel and often by consultants under contract to DEC. Unless special arrangements are made, these samples should be submitted Monday through Friday between 7:45 a.m. and 4:00 p.m. and relinquished to the Laboratory Supervisor or his designee.

Overnight Courier or package delivery service – This method may be used by non DEC personnel sampling for DEC program or a non DEC program, which contracts with DEC for laboratory service. Thermal preservation **must be** maintained by packing samples with a sufficient volume of ice (blue ice does not cool samples sufficiently). Unless special arrangements are made, overnight delivery is required and samples need to arrive Monday through Friday before noon. Samples sent by a package carrier, e.g. UPS or Priority Express, are to be addressed to:

UVM
Hills Agriculture & Science Building – DEC LAB
105 Carrigan Drive
Burlington, VT 05405
Attn: D.E.C. Chemistry Laboratory Supervisor

7.2.4 Sample Custody Procedures

- The Laboratory Supervisor must be given advance notice of samples requiring Chain of Custody handling procedures.

- Field personnel must document in a field notebook all details regarding sampling activities. Documentation must include exact information regarding date, time, location, names of people present, unusual events, field measurements, details of sample storage and security, and transfer of samples to others.

- Field personnel are supplied with the proper sampling containers, chemicals for sample preservation, coolers, sample labels, Chain of Custody sealing tape, a Chain of Custody Record from (Section 7.2.9): A listing of acceptable hold times, sampling procedures, and preservation techniques is provided upon request.

- Field personnel must collect samples according to standard procedures and add preservative if required. Samples requiring field preservation must be collected in containers containing the preservative. Field personnel needing to break the seal(s) at the laboratory to add preservation chemicals are asked to transfer custody to the laboratory after the samples are resealed. Lab personnel must be notified if preservation is to be done at the Lab by laboratory staff.

- Field personnel must seal the top of the sampling container with a Chain of Custody Sample Seal, initial the seal, complete the identifying label and store and transport samples in a sealed cooler with ice, if thermal preservation is required. A secure container capable of being sealed is acceptable if thermal preservation is not required.

- At no time are samples to be left unattended unless they have been locked or secured with initialed seals in place.

- The samples must be delivered to the Laboratory Supervisor or designated staff chemist who will accept the samples and perform the following steps.

    - verify that correct containers were used and required preservation was performed.
    - if thermal preservation is required:
        - verify that samples arrived on ice and cooling has begun
        - record the temperature of a representative sample.
    - verify that all samples listed on the Chain of Custody Record form are accounted for.
    - verify that all containers are properly sealed and that all seals are intact and the Chain of Custody form and seals are completed correctly.
    - accept the samples and sign, date and note the time in the appropriate Chain of Custody Record form space.
    - log samples into the LIMS and designate the samples as **enforcement** on the "Order ID Entry" page of the login. Label the samples with a LIMS generated label or verify that sample login was completed correctly and samples are properly labeled with unique sample identification numbers.

- store samples in a designated locked refrigerator(s) – Room015, volatiles must be kept in a separate unit if contamination is possible.
- provide the designated individual with the Chain of Custody Record form, to file.
- notify analysts or technical directors responsible for the analysis of the sample(s).

7.2.5 The Chain of Custody Record

Sampling personnel or the Project Officers are required to complete all items on the form prior to submitting samples (See Section 7.2.9, Chain of Custody Record form).

- The Project Name and Number are assigned by the Project Officer.

- The sampler(s) and/or witness are required to sign the form when samples are collected. A witness is not required to be present during sampling to satisfy the Chain of Custody requirements of sampling.

- Enter the name of the laboratory performing the analysis.

- The sample location is exactly the same information put into the "Customer Sample ID" field when samples are logged into the Laboratory Data Management System.

- Record the date and time of sample collection and whether the sample was a composite or grab.

- The description and number of containers should include the tests to be analyzed by groups on the slanted lines and the number of containers for each group in the accompanying box; e.g. volatiles, metals, semivolatiles on the slanted line and the number of containers/sample in the box.

- The total number of sample containers per location and any remarks regarding the sample should be recorded.

- When custody is transferred from one person to another, both parties must sign and date this form. If someone other than the person whose signature appears at the top of the form transports the samples to the laboratory, that transfer must be documented on this form.

- If the sample is to leave the laboratory for any reason the sample must be resealed and a Chain of Custody Record form will be reinitiated.

7.2.6 Responsibility of the Analyst

An analyst assigned to perform the required analyses on Chain of Custody samples is expected to follow the procedures listed to insure that the Chain of Custody is maintained throughout the analytical process.

- That analyst, using a Sample Sign-out Sheet, signs a Chain of Custody sample from the refrigerator, removes the container, breaks the seal and removes an aliquot of sample, which is adequate to perform the analyses requested. A majority of containers are designed to provide enough sample for one analysis or a series of similar analyses. This assumes that the sample will not be analyzed by another laboratory. If enough sample for a valid retest remains in the container after the analyst removes an appropriate aliquot of sample, the container is returned to the Chain of Custody refrigerator for possible re-analyses. An analyst, who is responsible for a subsequent analysis to be performed on an aliquot of this sample, must also document the removal and return of the sample on the sample sign out sheet. If all analyses from the container are complete any remaining samples are placed into long-term storage (Section 7.2.7). Empty containers and containers of samples in which insufficient volume remain to complete another analysis are discarded. If the client requests that samples be removed from the Laboratory facility the samples will be resealed and a new Chain of Custody Record will be initiated.

The specific steps to be documented on the Sample Sign Out Sheet are:

- Laboratory ID #.
- Date and time samples are removed from the refrigerator.
- Amount of sample removed.
- Initials of analyst removing the samples.
- Tests to be performed.
- Can a valid analysis be performed on the remaining sample Y/N? If N, then the remaining sample can be discarded. If Y, the sample is returned to the locked refrigeration unit.
- Date and time samples are returned to the refrigerator.
- Initials of analyst returning the container to the refrigerator or discarding vessel if insufficient sample volume remains.

7.2.7 Long Term Storage of Chain of Custody Samples and Records

When all tests on a sample from a particular container have been completed and if any remaining sample in that container can be used to obtain a valid analysis, that container must be stored as a Chain of Custody sample. Unless the laboratory has been specifically instructed to retain the samples by the Project Manager, the samples can be removed from the refrigerator and discarded once hold times for the individual analyses in that container have been exceeded by 30 days

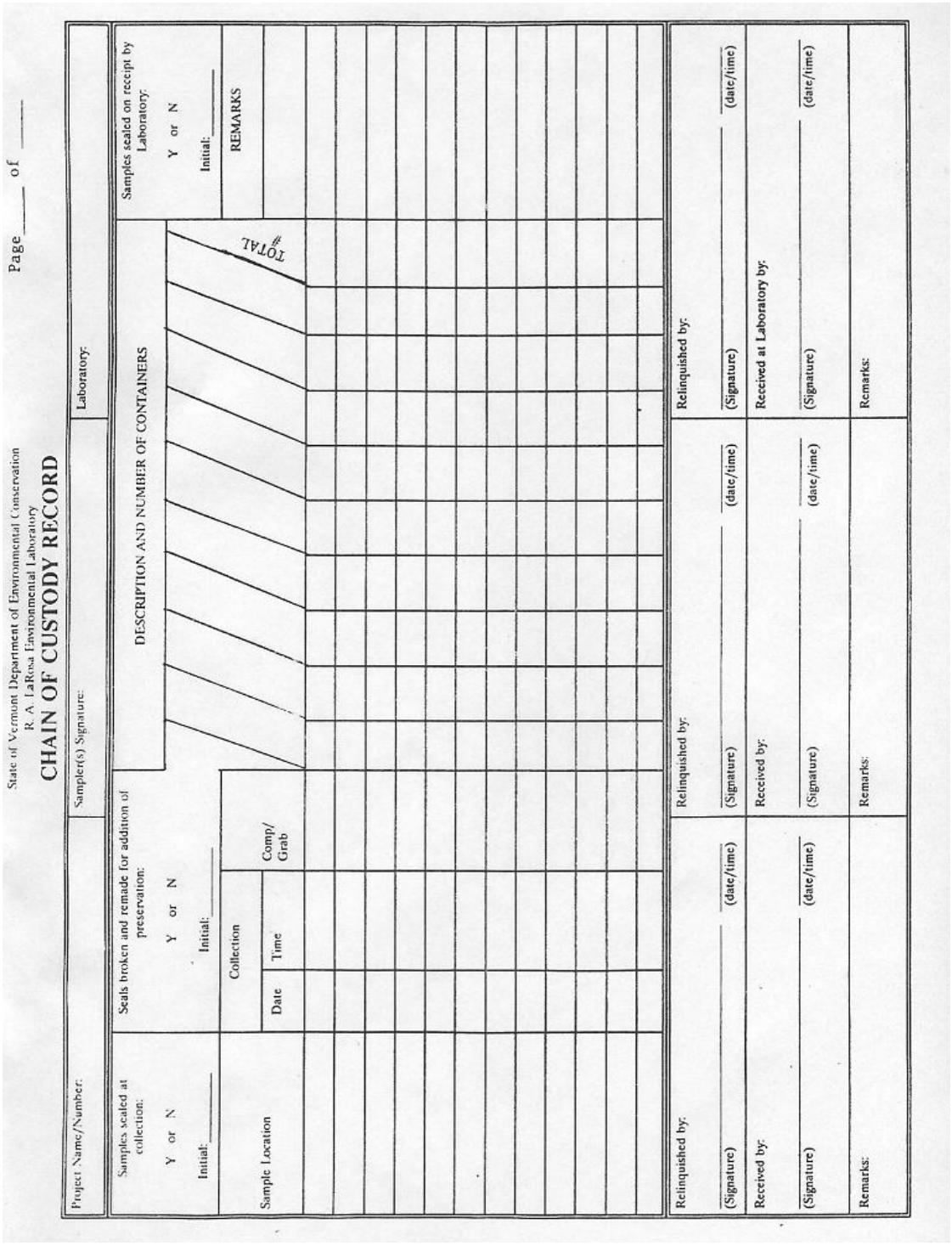
All paperwork with the exception of field notes, which are kept by the program responsible for the site, are retained by the laboratory until deemed unnecessary. The normal record retention is five years. All laboratory records must be kept secure and in confidence to the client. Laboratory

policy on record retention described in Section 10.0 Data Reduction, Validation, Reporting, Tracking and Storage must be followed.

7.2.8 Sample Containers, Preservation and Hold Times

Required containers, preservation and hold times for regulated contaminants are listed in Table 6.1 of the Laboratory's Quality Assurance Plan.

7.2.9 Chain of Custody Record Form



State of Vermont Department of Environmental Conservation
R. A. LaRosa Environmental Laboratory

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CHAIN OF CUSTODY RECORD

Project Name/Number:		Sampler(s) Signature:	Laboratory:

Samples sealed at collection: Y or N Initial:_____	Seals broken and remade for addition of preservation: Y or N Initial:_____	DESCRIPTION AND NUMBER OF CONTAINERS	Samples sealed on receipt by Laboratory: Y or N Initial:_____

Sample Location	Collection Date	Collection Time	Comp/ Grab	TOTAL #	REMARKS

Relinquished by:	Relinquished by:	Relinquished by:	
(Signature) (date/time)	(Signature) (date/time)	(Signature) (date/time)	
Received by:	Received by:	Received at Laboratory by:	
(Signature) (date/time)	(Signature) (date/time)	(Signature) (date/time)	
Remarks:	Remarks:	Remarks:	

8.0 Calibration Procedures

All instruments and equipment used within the Laboratory are routinely calibrated by Laboratory personnel. Many small instruments and measurement devices are also annually calibrated by an external calibration service following ISO 17025 protocol. A summary of calibration procedures for individual instruments and tests is provided in this section. Information is summarized in Table 8.1 Calibration Frequency, Procedures, Standards and Acceptance Criteria for Major Measurement Systems. Detailed calibration and continuing instrument calibration verification procedures are described in Laboratory Standard Operating Procedures (SOPs).

Primary Calibration Standards used for calibration are purchased from a reputable dealer or prepared at the Laboratory using reagent grade material. All purchased primary standards are certified by the vendor for purity and identity and when available are NIST traceable. Vendor supplied Certificates of Analysis are retained within analytical centers for a minimum of 5 years. Calibration Standards (working standards) are dilutions or mixtures of stock standards used to calibrate an instrument. These standards are prepared or restandardized frequently (Section 9.3).

Second source standards are routinely used to validate primary calibration standards, technique and methodology and when available are in the same matrix as the samples being analyzed. They are purchased or prepared from a different source than that used in the preparation of standards for use in the standard curve and are analyzed immediately following calibration. NIST traceable reference materials are used when available. Certificates of analysis are retained in analytical centers for a minimum of 5 years.

To insure that instruments remain calibrated throughout analysis, it is Laboratory practice to run a second source standard or a mid-range primary standard after every 10 samples for extended runs and after the last sample analyzed. Acceptance criteria for the continuing calibration check is generally ±10% but does vary between tests.

The calibration range defines how results are reported and samples are processed. Results below the low calibration standard are reported as less than (<) the Reporting Limit (PQL). Under some situations a client may request data below the low standard. In these situations data is qualified. Results above the high calibration standard must be diluted and reanalyzed so that the instrument reading is within the calibration range. If under an unusual circumstance a result is reported that is outside the calibration range the data is qualified. If a referenced method allows the use of a linear dynamic range, results above the high standard but within the established range can be reported without qualification. Method specified criteria for establishing and verifying the linear range must be met.

The 2009 TNI Standard (Chapter 5; Chemical Testing; Technical Requirements,Section 1.7.1 Instrument calibration) outlines the essential elements for the selection of appropriate instrument calibration techniques. Lab staff are required to familiarize themselves with the guidelines to assure that Laboratory calibration

procedures meet the TNI standard at a minimum. Referenced methods and Laboratory protocols may be more stringent then TNI standard requirements (Appendix B).

8.1 Organics

8.1.1 GC (Volatiles, Total Petroleum Hydrocarbons – DRO, Total Volatile Hydrocarbons – GRO)

An initial calibration curve is prepared for each analyte of interest. Five or more calibration standards are prepared with one of the concentrations at the lower reporting limit (PQL)and the other concentrations corresponding to the expected range of concentrations in field samples. Calibration Blanks are not used to establish the zero. Each standard is injected into the instrument and the area response is tabulated against the concentration. The average response factor or coefficient of determination is calculated for each curve by the software and is used to judge the curve fit. A avg. response factor $\leq$ 20% or a coefficient $\geq$ 0.99 is acceptable. The initial calibration curve must be verified every 12 hours (continuing calibration) by the injection of a mid-range standard. If the response for any analyte varies from the predicted response beyond the acceptance criteria, a new calibration curve must be prepared for that analyte. If data associated with any failed criteria is reported it must be qualified to alert the client of the Irregularity. Acceptance criteria is listed by method in Table 8.1.

8.1.2 GC/MS (Volatiles)

An initial calibration curve is prepared for each analyte of interest. Five or more calibration standards are injected with the lowest concentration at or below the lower reporting limit. The calibration curve is not forced through zero. Response factors (RF) are calculated for each target analyte relative to the internal standard that has a retention time closest to the analyte being measured.

$$RF = \frac{A_s \times C_{IS}}{C_S \times A_{IS}}$$

A_s = peak area of analyte or surrogate
A_{IS} = peak area of internal standard
C_s = concentration of the analyte or surrogate
C_{IS} = concentration of the internal standard

Mean response factors and mean relative standard deviation are calculated. Mean RSDs should be $\leq$20% for each target analyte. Minimum RFs for each calibration level should meet Method 8260C Table 4 Criteria. If the lowest calibration standard cannot meet criteria, PQLs should be adjusted if corrective actions cannot increase the RF. Unacceptable calibrations must be evaluated prior to proceeding and data flagged if RSD and minimum RF criteria are not met. If more than 10% (5 parameters) fail the 20% RSD limit or minimum correlation coefficient of .99 criteria analyses may not proceed. The following alternative calibration methods are described in Method 8000C and may

be used but must be used consistently.

- Linear regression. Acceptance Criteria: coefficient of determination (COD or C_f) $\geq$.99.
- Quadratic fit (six standards required). Acceptance criteria: coefficient of determination of (COD or C_f) $\geq$.99.

If unable to meet acceptance criteria using alternative calibration curves use the %RSD criteria and flag all data for failed parameters reported off this curve with "E" Estimated Value. Internal standard area responses must be within -50% to +100% of midrange standard. Verification of Initial Calibration must be done by running a second source (ICV Mid). Recovery limits are 70-130%. Quantitative analysis should not proceed for those analytes that fail unless all data is qualified. Calibration Verification must be performed at the beginning of each 12 hour shift (8260) or ever 24 hours (TO15). (After the Initial Calibration criteria have been met.)

The mass assignments of the GC/MS system are determined by calibration with perfluorotributylamine (PFTBA). The system is then hardware tuned to meet method criteria for mass spectra of a 50ng injection of BFB (4-bromofluorobenzene).

8.1.3 HPLC (carbonyl compounds)

An initial calibration curve is prepared for each analyte of interest. Five or more calibration standards are injected with one of the concentrations at the practical quantitation limit and the other concentrations corresponding to the expected range of concentration in real samples. Each standard is injected into the instrument and the area response is tabulated against the concentration. The coefficient of determination is calculated for each curve by the software and used to judge the curve fit. A coefficient above 0.999 for at least 3 of the 4 compounds and $\geq$0.995 for one is acceptable. The initial calibration must be verified every 10 injections by running a mid-range standard.

8.2 Metals

8.2.1 Mercury Cold Vapor Analyzer

Instrument calibration for mercury analysis is performed prior to the analyses of samples. A multi point curve is generated. A blank is one of the calibration points (zero) and the zero point is used to calculate the correlation coefficient. The zero instrument response is subtracted from all standard responses including the zero. The low standard concentration is at the Laboratory reporting limit. The calibration curves must have correlation coefficients greater than or equal to 0.995. Calibration verification is monitored by analyzing a second source standard immediately following calibration (Initial Calibration Verification - ICV). A mid-range standard is analyzed after every tenth sample, and at the end of the sample run to assure that calibration is maintained throughout the run (Continuing Calibration Verification -CCV). The calibration blank is also reanalyzed immediately following calibration, after every ten samples and at the end of the analytical run. Calibration blank results should be less than one-half the reporting

limit (PQL). The ICV result should be within ±10% of the true value for analysis to continue or data must be qualified. The CCV result(s) must be within ±10% of the initial value. Failure of a CCV sample requires recalibration or reanalysis of all samples analyzed after the last passing CCV.

8.2.2 ICP-MS

The instrument is tuned with multi-element tune solutions to meet method criteria. A daily performance report verifies thermal stability, selectivity and mass calibration. If the performance report fails the analyst needs to determine, based on the failed parameter(s), how to continue. The detectors are cross calibrated following detector maintenance/replacement, or when the correlation between pulse counting and analogue detection does not meet acceptance criteria (±15%).

After the performance report criteria are met a calibration curve is prepared for each metal to be analyzed daily or for each separate analytical run, whichever is more frequent. Four or more multi-element standards are analyzed to create a calibration curve. A blank is the zero point on the calibration curve and is used in the correlation coefficient calculation. One of the concentrations is at the reporting limit and the other concentrations correspond to the expected range of concentrations in samples to be analyzed. The correlation coefficient of linearity must be >.998. The calibration curve is verified by analysis of a mid-range second source standard (ICV) containing all the metals to be quantified.

Calibration is verified at the beginning of the run, after every 10 samples, and at the end of the run by analysis of a mid-range standard. Results should be within ±10% of the expected value.

If results are reported outside the calibration range the instrument's linear dynamic range (LDR) is established and verified every six months or when any significant change has been made to the instrument hardware. Sample analyte concentrations that are within 90% of the established LDR limit may be reported without dilution. Concentrations greater than 90% of the determined upper LDR limit must be diluted and reanalyzed.

The upper limit of the LDR is established for each isotope utilized for reporting by determining the signal responses from a minimum of three different concentration standards across the range. The standards are prepared, analyzed and quantitated against the normal calibration curve. The data and calculations for the choice of the range is documented and kept on file.

8.2.3 ICP

Instrument calibration for ICP analysis is performed prior to the analyses of samples. Four or more multi-element standards are analyzed to create a calibration curve. A blank is the zero point on the calibration curve and is used in the correlation coefficient calculation. The low standard concentration is at the laboratory reporting limit (PQL). The calibration curves are linear with no weighing and must have correlation coefficients

greater than or equal to 0.998. Calibration verification is monitored by analyzing a second source standard immediately following calibration (Initial Calibration Verification – ICV). A mid-range standard is analyzed after every tenth sample, and at the end of the sample run to assure that calibration is maintained throughout the run (Continuing Calibration Verification – CCV). The calibration blank is also reanalyzed immediately following calibration after every ten samples and at the end of the analytical run. Calibration blank results should be less than one-half the reporting limit (PQL) and the ICV result should be within ±10% of the true value for analysis to continue or data must be qualified. The CCV result(s) should be within ±10% of the initial value. Failure of a CCV sample requires recalibration or reanalysis of all samples analyzed after the last passing CCV.

8.3 Inorganic Chemistry

There are several automated and non-automated analyses performed in the inorganic chemistry section. Calibration and calibration verification protocol will vary from test to test. For most tests calibration is verified by the analysis of a second source standard (ICV) at the beginning of the analytical run. The Initial Calibration Verification (ICV) should be within $\pm$ 10% of the true value for analysis to continue. A mid-range Continuing Calibration Verification standard (CCV) is analyzed after every 10 samples. A low level CCV or LCS is also analyzed within the run. Results should be within established control limits.
For most colorimetric analysis a standard curve consisting of 4 to 6 points and having a correlation coefficient of at least .995 is generated. Auto Analyzer methods have a blank as one of the calibration points. The blank is included in the correlation coefficient calculation. A typical ion chromatography run will have a standard curve consisting of 4 or 5 points for each ion of interest. Ion chromatography calibration curves include a blank as part of the calibration. The curves are not forced through zero. Combined anion calibration standards are prepared from stock standards. The correlation coefficient of the standard curve for each ion should be >.995. The coefficient is calculated by plotting the peak area against the standard concentration using a linear fit.

8.4 Support Equipment

8.4.1 Thermometers

Thermometers used in the Laboratory are calibrated against a NIST-traceable thermometer. The NIST thermometer is re-certified every 5 years. Correction factors are taken into consideration when the thermometer is used to determine correction factors of Laboratory thermometers. Correction factors are noted on thermometers if needed. Correction factors, date calibrated, temperatures of both thermometers and thermometer serial numbers are documented in a laboratory notebook. Infrared thermometers which are used to check sample temperatures of incoming samples, are verified annually by comparing the reading against a NIST certified thermometer placed in a bottle of refrigerated water. The IR gun should read within 0.5°C of the calibrated thermometer.

8.4.2 Refrigeration Units

Temperatures within refrigeration units are checked on days the laboratory is open. A designated back-up will monitor the units if the primary monitor is absent from work. It is expected that there will be occasions when the units are not monitored but this should not exceed more than 2 days/month. Temperatures are recorded in a logbook and should be 0-6°C for refrigeration units and -17° C $\pm$ 2° for freezers. Thermometers are submersed in an appropriate solution within each unit. If temperatures exceed these limits the unit is monitored and corrective action taken if temperatures remain outside limits.

8.4.3 Incubators/Water Baths/Ovens

Microbiology incubator temperatures are checked twice daily when in use. Temperatures must remain within method specified limits. Oven temperatures for tests requiring a specified temperature are checked daily when in use. All temperatures are recorded. The water bath used for the digestion of mercury samples is checked and temperature recorded at the beginning of analysis, and at the end of the digestion and must be 95° $\pm$ 2° C.

8.4.4 Balances

Calibration of analytical balances is performed annually by a calibration service that is ISO 17025 compliant. Calibration is verified on days the laboratory is open with NIST traceable Class 2 weights. A designated back-up will monitor the units if the primary monitor is absent from work. It is expected that there will be occasions when the units are not monitored but this should not exceed more than 2 days/month. Two weights bracketing the expected range of measurements are used, measurements should be within ± .5mg. All weights are recorded in a lab notebook. Weights used to verify calibration at the Laboratory are Rice Lake Weight Kit - ASTM Class 2, 100g - 100mg.

The weights are annually verified internally. Weights are cleaned with 95% ETOH 24 hours before they are checked. The balance used to verify the weights is calibrated by an external calibration service within 48 hours in the weight check. Weights must be within the balance tolerance of ± .0003g or the weight tolerance, whichever is greater. Periodically weights may be sent to an external calibration service for verification.

8.4.5 Automated Pipettes and Dispensing Devices

Multi-volume dispensing devices have each dispensing head calibrated at a minimum of two volume settings each. TNI requires that all class “A” dispensing devices be checked on a quarterly basis. This is performed in-house.

8.4.6 pH Meters

A two point calibration is performed daily and after every 2 hours of continued use. Standards bracket the pH of the samples analyzed. The percent slope of the calibration

curve must be >97%. A third pH solution with a pH bracketed by the two calibrants is analyzed to verify calibration. A third pH solution may also be used to verify an occasional sample that measures outside the calibration curve rather than recalibrating the meter. The calibration check solution pH must bracket the sample and must read within ± .05 pH units of the true value. If criteria is not met the meter must be recalibrated using appropriate standards.

8.4.7 Computer Software

Computer software is purchased either to support new instrumentation, to upgrade the performance of existing equipment or to manage the tracking of Laboratory data. Software needs to meet bid specifications which is demonstrated during installation/or training. The IDA files contain relevant data that documents performance.

Table 8.1 Calibration Procedures, Frequency, Standards and Acceptance Criteria for Major Measurement Systems

Instrument/Analytes	Procedure	Frequency	Standard[a]	Acceptance Criteria[b]
AA Spectrophotometer -mercury (cold vapor analysis)	Calibration (4-5 point).	Daily or failure of ICV/ CCV.	Vendor Certified Standard. Plasma grade-ICP	Correlation Coefficient >0.995
	Second Source Standard ICV (1 point).	Immediately following calibration	Certified Second Source Standard	±10%
	Primary Calibration Standard (CCV) (1 point).	Following ICV after every 10 samples and at end of run.	Mid-Range Calibration Standard	±10%
ICP - metals	Calibration (>4 points) including blank standard	Daily or failure of ICV/CCV	Vendor Certified Standard	Correlation Coefficient >0.998
	Initial Calibration Verification Standard (ICV), (each analyte near the mid range of calibration)	Immediately following calibration	Vendor Certified Second Source Standard	±10%
	Continuing Calibration Verification Standard (CCV), (each analyte near the mid range of calibration)	Following calibration, after every 10 samples and at end of run	Vendor Certified Primary Source Standard	±10%
ICP-MS -metals	Performance Report Verifies -thermostability -sensitivity -mass calibration	Prior to each daily analytical run	Tuning Solution	Mass Calibration Verification: max peak error ±0.1amu., min & max, peak width 0.65-0.85amu Acquisition Parameters: RSDs for 7Li, 115In, 238U *should* be <2%; count rates *should* be: 7Li >40000, 115In >400000, 238U >400000; ratio results: *should* be: 156 CeO/140Ce <0.02 138Ba++/138Ba <0.03
	Manual or Auto Tune	Required upon failure of a Performance Report when not related to peak width failure	Tuning Solution 10 elements at 10 µg/L	Countrates *should* be: 9Be>7000, 115In>200000, 238U>400000; ratio results *should* be: 138Ba++/138Ba<0.03, 156Ce O/140Ce<0.02
	Detector Cross Calibration	When the correlation between pulse counting and analog detection requires improvement due to drift, maintenance, mass calibration, etc.	Tuning Solution (62 elements at 5 – 1250 µg/L), or Tune D Solution (24 elements at 10 µg/L)	Passes performance test following detector cross calibration
	Mass Calibration	Upon failure of peak width and/or peak error that cannot be corrected by an instrument tune or cross calibration	Tuning Solution (62 elements at 5 – 1250 µg/L), or Tune D Solution (24 elements at 10 µg/L)	Max peak error ±0.1 amu, min & max peak width 0.65 – 0.85 amu

Instrument/Analytes	Procedure	Frequency	Standard[a]	Acceptance Criteria[b]
ICP-MS -metals (continued)	Peak Resolution Adjustment	Required upon consecutive peak width failure from performance report that can not be corrected by procedures above	Tuning Solution 10 elements at 10 µg/L	Peak width 0.65-0.85amu
	Calibration (>4 points) including blank standard	Each separate analysis	Vendor Certified Standard	Linearity >0.995, value within ±10%
	Initial Calibration Verification Standard (ICV), (each analyte near the mid range of calibration)	Immediately following calibration	Vendor Certified Second Source Standard	±10%
	Continuing Calibration Verification Standard (CCV), (each analyte near the mid range of calibration)	Following calibration, after every 10 samples and at end of run	Vendor Certified Primary Source Standard	±10%
Ion Chromatograph -nitrate-N -chloride -sulfate -nitrite-N	Calibration (3-5 points).	Daily or failure of ICV/CCV.	Vendor Certified Standards	Correlation Coefficient $\geq$ 0.995
-fluoride	Second Source Standard ICV	Immediately following calibration	Certified Second Source Standard	±10%
	Primary Calibration Standard (1 point)	Immediately following ICV after every 10 samples and end of run.	Mid-range Calibrant	±10%
Autoanalyzer -ammonia -chloride -nitrate/nitrite -nitrogen (total) -phosphorus (total, -ortho) -silica -TKN	Calibration (5-6 point).	Daily or failure of ICV/CCV	Reagent Grade Chemicals or Vendor Certified Standards	$\geq$0.995
	Second Source Standard (ICV).	Immediately following calibration	Certified Second Source Standard	±10%
	Primary Calibration Standard (CCV)	Following ICV after every 10 samples and at end.	Mid-Range Calibrant	±10%
	Cadmium Column Check (nitrate/nitrite only)	Beginning and end of run.	Nitrite Standard (mg/l)	±10% of True Value
GC: Diesel Range Organics (DRO) (8015)	Calibration (5 point).	Initially or upon failure of CCV.	Vendor Certified Standard	Coefficient of Determination >0.99
	Second source standard. (ICV)	After initial calibration.	Vendor (different from calibration) Certified Standard.	±20%
	CCV	Every 12 hours	Mid-point Standard	±20%
Volatiles (8021)	Calibration (6 point).	Initially or upon failure of CCV.	Vendor Certified Standard	Coefficient of Determination >0.99

Instrument/Analytes	Procedure	Frequency	Standard[a]	Acceptance Criteria[b]
	CCV	Every 12 hours.	Mid-point Standard	±20%
	Second source standard. (ICV)	Immediately after calibration.	Vendor Certified Standard.	±20%
Volatiles – Gasoline Range Organics (GRO)	Calibration (6 points)	Initially	Gasoline standard	Coefficient of Determination >0.99
	Second Source Standard (ICV)	After initial calibration.	Mid-point of calibration curve.	±30%
	Continuing Calibration Verification.	Every 12 hours.	Mid-point standard.	±30%
GC/MS: Volatiles(8260/TO15)	Instrument Tune	Every 12 hours (24 hours for TO15).	BFB	Method Specified Criteria
	Calibration (5-6 points).	Initially and upon failure of CCV.	Vendor Certified Standard	Method Specified Criteria (See Section 8.1.2 for details.)
	Second Source Standard	After initial calibration	Vendor Certified Standard	□30% Difference from Initial Calibration. (See Section 8.1.2 for details.)
	Continuing Calibration Check (CCV)	Beginning of each batch	30ppb standard used to make curve (TO15 1ppb).	□30% Difference from initial calibration (TO15) 20% for 8260. (See Section 8.1.2 for details.)
HPLC (TO11)	Calibration 7 points.	Initially, upon failure of CCV or every 3-4 months.	Vendor Certified Standard	Correlation Coefficient >.999 for 3 of the 4 compounds and ≥ 0.995 for the other.
	Second Source Standard	After initial calibration and at the beginning of each run.	Vendor Certified Standard.	±15% difference.
	Continuing Calibration Check (CCV)	Every 10 samples and at end of sequence.	Mid-point standard of curve.	±15 Percent Difference
pH Meter -pH -alkalinity	Calibration (2 point)	Daily	Vendor Certified Buffer	% Slope □97%
	Second Source Standard or Different Lot #	Daily	Vendor Certified Standards	± .05 pH units
Conductivity Meter -conductivity	Calibration (4 points).	Annual	ACS Grade Reagent Standards	±10% of Certified Values
	Second Source Standard (2 levels).	Daily	Vendor Certified Standards	±10% of Certified Values
Spectrophotometer -COD	Calibration (9 point)	Bi-Annually	Vendor Certified Standard	Correlation Coefficient >0.995
	Second Source Standard	Daily	Certified Reference Material	±10
Turbidity Meter -Turbidity	Calibration (3 NTU Levels)	Quarterly (minimum)	Primary Calibration Standards	±10%
	Calibration Check (2 NTU Levels)	Daily	Secondary Standard	±10%
Dissolved Oxygen Meter -BOD	Barometric Pressure Calibration	4 Hours	Barometer	
Fluorometer -chlorophyll	Calibration (4 point)	Bi-Annually	Pure Chlorophyll A	± 10%
	Calibration Check (2 point)	Daily	Solid Chlorophyll A Secondary Standard	±10%

Instrument/Analytes	Procedure	Frequency	Standard[a]	Acceptance Criteria[b]
Analytical Balances	Calibrated according to manufacturers instructions.	Daily		Manufacturer Specified
	2 Point Check	Daily	Class 2 Weights	±0.5mg or ±5 mg (depending on balance)
Thermometers	1 or 2 point verification	1/year	NIST Traceable Thermometer (Verified every 5 years)	Correction Factor no greater than 3°

[a] Standards are traceable to National Standards when available.

[b] If sample values are reported from an analysis where acceptance criteria are exceeded an appropriate remark code or sample note should be entered to justify reporting of the results.

9.0 Analytical and Operational Procedures

9.1 Analytical Methods

All methods commonly used at the DEC Laboratory are EPA approved. Parameters by matrix with corresponding method numbers and references are summarized in Table 5.1 of this manual. Current Laboratory Standard Operating Procedures (SOPs) are available upon request. A list of Laboratory SOPs can be found in Appendix A. Technical SOPs describe in detail, routine analytical tasks performed at the Laboratory and typically include:

- Identification of test method
- Applicable matrix or matrices
- Method detection limit (MDL) / limit of quantitation
- Scope and application
- Summary of test method
- Definitions
- Interferences
- Safety
- Equipment and supplies
- Reagents and standards
- Sample collection, preservation, shipment and storage
- Equations, calculations and data reduction procedures
- Quality control
- Calibration and standardization
- Procedure
- Calculation
- Method performance
- Pollution prevention
- Data assessment and acceptance criteria for quality control measures
- Corrective actions
- Contingencies for handling out of control or unacceptable data
- Waste management
- References
- Any tables, diagrams, flowcharts and validation data

Non-analytical Standard Operating Procedures are documented in the following Laboratory manuals or SOPs:

- VT DEC Laboratory Safety Manual
- VT DEC Glassware Washing SOP
- Deionized Water System Maintenance SOP

9.1.1 Method Review

SOPs for current methods should be reviewed by the primary analyst at least biannually, signature on cover page signifies document review and/or that it has been revised. Upon

completion of the review the SOP is signed and dated in blue ink. The most current revision of the referenced method should be part of the review process to assure that all method requirements are being met and any deviations from the referenced method are documented. Also, the bench copy should be part of the review process, so as to incorporate any changes to the procedure or document. Review is documented by signing and dating SOP. If changes warrant a new revision number, these revisions must be documented at the end of the SOP. The final signature page in the SOP is for documentation of secondary analyst has read, understands and agrees to follow SOP.

9.1.2 Method Review/Revision

If a significant variation to a referenced method is made the Laboratory must first demonstrate the alternative protocol results are comparable. The Laboratory SOP must clearly describe the variance and comparability data must be on file at the Laboratory. To demonstrate comparability the Laboratory must, at a minimum, analyze four consecutive representative split sample(s) using the standard method and the alternative protocol. The alternative protocol results must be within 10% of the approved test procedure. Each sample site may be subject to this demonstration of comparability.

The analyst's bench copy (Control document 1 of 1) is placed in respective laboratory or section after review, ensuring most recent SOP is available incorporating any changes. Significant changes, such as any change in the calibration or procedure, must be authorized (initialed and dated) by the Lab Supervisor, and constitutes a new revision. Minor changes or corrections do not need a new revision number. The primary analyst is responsible for reviewing their SOPs and the referenced method should be used to assure that all method requirements and criteria are being met. The QA Officer and Laboratory Supervisor perform second level review prior to approval. The laboratory maintains a total of two paper copies, "Original" kept by QA Officer, and "Control document 1 of 1" which is kept in respective lab or section for easy reference, in addition to the electronic copy kept by laboratory supervisor. When an SOP is requested for revising, the QA Officer places it on the "Y drive" for a specified time. It is not to be copied to any other drive. Once completed and all secondary review and signatures are obtained, the "Original" and "Control copies" are replaced in laboratory. All signatures will be in blue ink for easy identification of "Original" or "Control copy 1 of 1". The QA Officer maintains copies (paper/electronic) of older SOP's for a minimum of 5 years.

9.2 Laboratory Water

Laboratory water meets or exceeds ASTM Type II Reagent Grade Water requirements. The laboratory's water system is described in the Laboratory Deionized Water System SOP. The SOP also provides a description of the daily, weekly, monthly and yearly water system maintenance and monitoring schedules.

9.3 Reagent Preparation, Documentation and Storage

All standards and reagents are prepared from reagent grade materials, primary standards or are purchased from reputable vendors. When standards are purchased the date of receipt is documented on the container and the certificate of analysis. Certificates are filed for a minimum

of five years. Standards and reagents are prepared using Class A volumetric glassware and calibrated dispensing devices and ASTM Type II reagent water.

An electronic log or log books are used to record the receipt of all vendor supplied standards and reagents. The vendor, date received, lot number, expiration date and other pertinent information must be documented in the Standards/Reagent Log. Log books or sheets are utilized to document all information needed to maintain proper traceability of all standards and reagents prepared or purchased by the laboratory. Logs document the date of preparation or opening of purchased standards, expiration date, a list of standards/reagents or solutions used, lot numbers and the preparer's name (initials). Additional information may also need to be recorded such as pH.

Once a solution is prepared it is labeled with the solution name or description, concentration or normality, preparation and expiration dates and initials of preparer. Documented information must be sufficient to allow traceability to the preparation record which should provide traceability of all ingredients.

Expiration dates for standards and reagents are usually specified in methods or by the manufacturer and are adhered to unless degradation prior to this date is observed. Purchased materials are labeled with the date received and opened and the expiration date if more stringent than manufacturer's expiration date. Reagents that do not have a manufacturer's expiration date will have a five year hold time entered into the Laboratory's electronic reagent log. Reagents will be evaluated after 5 years. Reagents are stored according to Method or manufacturer's instructions and discarded upon expiration. All prepared 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. Clean disposable pipette tips are used to remove stock standards from original containers. If degradation becomes apparent the solution is discarded immediately and holding times are reduced. When expiration dates are not specified the following guidelines are used:

Stock Standards used for calibration can be used for 1 year if properly preserved and stored.

Titrating Solutions need to be either re-standardized or a new bottle of vendor certified standard opened each month. Titrating solutions used by the Lab include .02N sulfuric acid (vendor certified to .0202 - .0198N) (Alkalinity) and .0375N (vendor certified .038-.037N) sodium thiosulfate (BOD, Dissolved Oxygen).

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.

9.4 Miscellaneous Procedures

In addition to method specific procedures several operational activities are monitored at the Laboratory. Documentation of the monitoring can be found in the following locations:

- Reagent and preparation notebooks
- Instrument maintenance logs
- Instrument service logs
- Laboratory water system maintenance logs
- Balance/refrigeration/incubator monitoring log books

9.5 Traceability of Measurements

All measurements are required to be traceable to a national or international standard of measurement when a traceable standard is available. Equipment and measurement devices including balances, thermometers, and dispensing devices, associated with the accuracy of a measurement are calibrated according to protocols outlined in this QA Plan. Reference standards and materials used at the lab or by equipment calibration services are traceability to a national or international standard. Traceability requires that lab employees document and retain all pertinent information related to a measurement. Records pertaining to calibration, calibration verification, and analysis must be detailed and traceable to the standards used. All results, information and calculations needed to generate a result must be documented. Record retention will vary depending on the record but must meet lab policy outlined in the QA Plan.

9.6 Data Recording and Editing

All written records in notebooks and on bench sheets need to be legible and recorded in permanent ink. Sharpies or other markers should not be used. Corrections must be made by drawing a single line through the incorrect entry. Corrections must be initialed and dated with the date the correction was made (month-day-year). Writing over an incorrect entry or using white-out, correction tape or erasers is not allowed. A reason for the correction must be provided if not obvious. Forms must be spacious enough to allow for legible corrections to be made, initialed, dated and a reason for the correction documented. The use of a code is acceptable if defined. Pages may not be removed from notebooks. All records must be signed or initialed (electronic or written signatures are acceptable) and the reason should be clearly indicated such as “prepared by”, “reviewed by” or “validated by”.

9.7 Document Changes

Significant changes to documents (SOPs, QAPLAN) shall be reviewed and approved by the laboratory supervisor and the QA Officer should be notified of approved changes.

The laboratory supervisor and QA Officer shall have access to pertinent background information upon which to base their review and approval.

Significant changes include, but are not limited to: change to calibration protocol, deviations from referenced methods.

All hand-written amendments shall be clearly marked, initialized and dated by the individual amending the document and the laboratory supervisor. A revised SOP must be formally reissued

as described in Section 9.1.2 of this document and SOP 6.2 Preparation of Technical Standard Operating Procedures.

10.0 Data Reduction, Validation and Approval, Reporting, Tracking and Storage

All analytical data generated by the DEC Laboratory is recorded, reported, reviewed and archived according to Laboratory protocols described in this Section of the QA Plan and in Laboratory SOPs. Analytical areas have slightly different data reduction, validation and reporting protocols depending on the means by which the data is generated and entered into the Laboratory Information Management System (LIMS) and specific method requirements.

10.1 Data Reduction

Data reduction is the process of transforming raw data into final results that are reported in standard units to Laboratory users. The Laboratory's goal is to minimize the steps needed to transform raw data into reportable results and maximize on the number of analytical results generated by automated systems and electronically exported into the LIMS. Fewer data transcription and calculation errors occur when the process is automated.

Laboratory SOP's include equations used to calculate results or a reference to the instrument manuals or methods that include the equations, the method of calculation and bench sheets used to record pertinent data. A second analyst verifies all manually calculated data. All calculations and information needed to recalculate the results must be documented.

10.1.1 Manual Integration

Situations arise where the automated quantitation procedures in the GC/MS, GC, HPLC and IC software provide inappropriate quantitations. This normally occurs when there is compound co-elution, baseline noise, or matrix interferences. In these situations, the analyst must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target compound, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet Quality Control (QC) criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Manual integration must be documented.

Where manual integration has been performed, most software will mark the integrated area with the letter “M” on the quantitation report. Removal of data computer operational codes, such as the “M” flag is not allowed. A hard copy print-out of the quantitation report will be filed with the modified report if an electronic copy cannot be archived. Standard Operating Procedures; 4.15 Standard Operating Procedure for Manual Manipulation of Computer Generated Data, describes laboratory policy in greater detail.

10.2 Data Validation and Approval

The analyst generating the analytical data has the primary responsibility for its correctness and completeness. It is his or her responsibility to verify that the instrument was calibrated and performing correctly. Analysts are responsible for analyzing the appropriate type and quantity of quality control samples with their daily work. Results must meet pre-established control limits. If control limits are not met the lead analyst is responsible for reanalyzing samples or documenting, justifying and flagging final analytical results or reported quality control data. If data is deemed unacceptable due to quality issues the data should not be reported. The Laboratory Supervisor must be notified and written notification must be provided to the client. The protocol for reporting data in which pre-established control limits are not met is described in Section 5.0 of this manual.

In some instances raw data is converted to reportable data and entered electronically from electronic spreadsheets or instruments into the LIMS Data is electronically transferred from instruments into the LIMS for ICP/MS, HPLC, IC, GC/MS, GC, and Lachat Auto-analyzer instruments. Prior to electronically transferring the data the primary analyst parses the data, creates a QC batch, reviews parsed data, selects results to be entered and assures that correct spiking and standard concentrations have been entered.

Validation of reported results by a second analyst is required. It is the responsibility of the primary analyst to assemble a data package containing all relevant raw data needed for data interpretation and validation for each batch of samples processed. All corrections must be properly initialed, dated and the reason for the revision documented. Data packages must include: extraction logs, bench sheets, instrument printouts such as quantitation reports, integrator peak area/height and retention time reports, chromatograms, modified and unmodified chromatograms when manual integration has been performed, and diagnostic reports when applicable. The second analyst validates the results for the QC Batch using the raw data contained in the data package. Results can not be approved or released until the validation step is performed. It is the data reviewer's responsibility to know the frequency and type of quality control samples required and acceptance limits for each method he/she is reviewing; including curve acceptance, continuing calibration and precision and accuracy criteria. If criteria are not met and data are not flagged the data reviewer must return the data to the analyst responsible for flagging results. The data reviewer must also assure that all hand corrections are properly documented. If the data reviewer feels the data should not be reported due to quality issues it is his/her responsibility to notify the technical director of the analytical center or the Laboratory Supervisor.

Once a second analyst validates the QC Batch the data is available for approval and release. The Laboratory Supervisor or his designee reviews and approves all data for a given sample before it is released. This final review insures that all QC reporting and data qualifying requirements were met and results from different parameters for a given sample correlate. The dates of data entry, validation, and approval and the name of the employee responsible for each step are tracked within the LIMS.

When an error in an approved report is found, the Laboratory Supervisor or his designee will direct the LIMS database administrator to unauthorize the official lab report(s). The Laboratory

Supervisor or his designee will make the changes and reapprove the report. If a revised report is necessary the client is contacted and notified that a revised report has been made available. Corrective actions must be identified and implemented when possible to prevent future occurrence.

Sections 10.2.1 through 10.2.3 describe the types of checks performed at data validation for each of the analytical centers. Method specific checks are being incorporated into SOPs as they are revised.

10.2.1 Organics

In the organic area each data set has a data review check off list that must be completed by a second analyst. The following information is verified when applicable. Method specific checks and acceptance criteria will eventually be detailed in each laboratory SOP.

- Checks all worksheet header information for completion. Checks dates (extraction, analysis and calibration and insures they are documented and entered into the LIMS.
- Checks initial calibration data against established criteria.
- All criteria for instrument tuning, internal standard areas, retention times, surrogate recoveries and analytical quality control results are checked.
- Checks all method quality control data to assure the correct type and amount of checks are performed and results are within control limits
- Compounds identified on the quantitation report must agree with results reported. All manual integrations must be properly documented and before and after manual integration chromatograms must be printed in sufficient detail to show the manual integration.
- All calculations such as total volatile hydrocarbons, soil concentrations, percent recoveries and dilutions are checked.
- Verifies that LIMS is correctly calculating reported results (when applicable) and correct standard concentrations and dilutions have been entered
- All irregularities are properly documented and if necessary data flagged when control limits or method acceptance criteria pre-established are not met.
- Verifies that sample dilution factors are accounted for in manual, instrument and LIMS calculations.
- Periodically verifies Excel or LIMS calculations to assure they are being performed correctly. Verifies all data entry into Excel spreadsheets used to calculate retention time windows or other Quality Control limits.

10.2.2 Inorganics/Metals

In the inorganic analytical center the second analyst checks the following items when applicable. Method specific checks and acceptance criteria will eventually be detailed in each laboratory SOP.

- Verifies that the analysis date, time and analyst initials are documented on bench sheets and then entered into the LIMS. (Time of analysis is required only if the sample hold time is $\leq$72 hours.)

- Insures all calibration and continued calibration criteria are met.
- Checks all method quality control data and documentation to insure the correct type and amount of checks are performed and results are within control limits and entered into LIMS.
- Checks all bench sheets for completion (i.e., chemical lot numbers, QC identification, initials, dates and times when required) and verifies that standards and reagents have not expired).
- Ensures accuracy of manual calculations and data to be parsed. Verifies that manual calculations, dilutions and raw data agree with imported data.
- Verifies that dilution factors have been properly accounted for and that standard and spike concentrations are correct.
- Checks to be sure any irregularity is documented and if necessary, data flagged when pre-established control limits are not met.
- If the data set was imported into the LIMS, at least 5% of results should be checked to be sure the import process was performed with out error. If the sample was diluted the data reviewer verifies that the correct data was exported.
- Periodically verifies Excel or LIMS calculations to assure they are being performed correctly.
- Verifies all manual data entry steps into LIMS or Excel programs.

10.2.3 Microbiology

Method specific checks and acceptance criteria will eventually be detailed in each laboratory SOP.

- Checks all Data Management System entries against bench sheets for transcription and reporting errors for manually entered information. All dilution calculations are checked. MPN values are rechecked against MPN Tables if the MPN Program has not been used.
- Insures that the date and time of analysis and the chemist initials are entered on bench sheets and into the LIMS.
- Checks for completion of required bench sheet information.
- Insures that documentation of the notification of appropriate contacts has been made when acceptance limits are exceeded for clients that require immediate notification.

10.3 Data Reporting

10.3.1 Policy

Laboratory staff shall not release results (electronic, paper or verbal) to individuals outside the Agency unless the Laboratory has been requested to do so. All inquiries for information must be directed to the Laboratory Supervisor who will either obtain written permission (e-mail is acceptable) or forward the request to a Program or Project Manager. All records are held secure and confidential.

10.3.2 Final Report Format

Data is transmitted to Laboratory users in one of two ways: PDF of an Excel table or paper reports for each sample group. Final reports for test data are issued only after internal review has been completed. Electronic transfer of data is an option available to laboratory users that have access to the laboratory network.

Electronic Reports do not contain all the information presented on paper reports. Clients receiving electronic reports are aware that a cover page with general and specific order comments is not provided. The information is retained and recorded in the LIMS (order comments) and is available.

If an order has both Organic and Inorganic tests requested two separate reports for the same order ID will be generated. The reports have a different format. The cover page of both reports may have Order specific comments that have been added by chemists or the laboratory supervisor.

10.4 Data Tracking and Record Storage

10.4.1 General Information

The Laboratory has policies and procedures for the retention and disposal of all quality and technical records (see Summary Table 10.1 Record Storage and Retention Times). The record keeping system allows for the reconstruction of all activities required to produce an analytical result. All records are stored under appropriate conditions for the type of media (electronic or hard copy), and are readily retrievable to individuals that are allowed access. Backup and access policies for electronic files are in place. Records must be legible and held secure and in confidence for a minimum of 5 years. Records may be destroyed after the minimum required hold times have been exceeded. The State of Vermont's policies and procedures for record retention and access will be followed.

10.4.2 Sample Handling and Receiving

Records are maintained for all procedures and policies pertaining to sample handling and receiving for a minimum of 5 years. Records of any deviations from policies are also retained either on bench sheets, in the LIMS or in both locations. Electronic records of LIMS sample receiving details described in *Section 6. Sample Handling*, are archived according to policy described in Section 10.4.3.2. Paper copies of Chain of Custody logs are permanently retained.

10.4.3 Technical Records

10.4.3.1 Paper Records

Original raw data for calibrations, samples and quality control measures, worksheets, instrument response records and vendor supplied standard certification paperwork are archived at the Laboratory 5 years after data is reported to clients as final. . Once the minimum retention period is met original

paper and electronic records are destroyed. The State of Vermont record Retention Policy for laboratory records is is described in the DEC Records Management Procedure fo the Monitoring General Records Schedule (GRS1000.1063). Analyst observations and calculations are documented at the time of analysis and retained with the raw data. All written records are documented in permanent ink. Errors in records must be corrected by drawing a single line through the error. The correct value is entered alongside the incorrect entry with the initials of the individual making the correction and the date of correction. When results are changed due to reasons other then transcription errors the reason for the correction must be obvious, if it is not the analyst must document why the documented result has been modified.
Laboratory reagent notebooks and maintenance logs (paper) are retained for a minimum of five years after last entry and cannot be destroyed without the Laboratory Supervisor's consent. The notebooks are stored within each analytical center and retained until no longer in use, plus 5 years, then destroyed. Information contained in notebooks includes sample processing steps and details such as: extraction and digestion records, instrument maintenance and routine checks, data reduction and transformation steps and standard and reagent receipt and preparations (if bench logs are not used).

Earlier revisions of Standard Operating Procedures (SOPs) and Quality Assurance Plans are archived (paper and electronic) until revised or no longer used, then retained for five year, then destroyed.. The document control system used in this QA Plan (upper right hand corner of page) is also used for lab SOPs
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10.4.3.2 Electronic Records

Electronic logs and bench sheets are stored as both paper and electronic copies in most instances. Electronic Logs raw data are periodically archived on CD. Records are retained until data is reported as final then retained for 5 years, and then destroyed.

The Vermont DEC Laboratory Information Management System (LIMS) data resides on the main DEC-SQL server. A full back-up of this server occurs every night Monday – Friday. The Friday night back-up includes verification. The daily tapes for Monday through Thursday are stored in the room in which the server is located. The weekly Friday tapes are stored in a fireproof file cabinet in a different building. Every fourth Friday a monthly tape is prepared and stored in a third building in a fireproof cabinet located in a locked room. All rooms used for storing the tapes are temperature controlled. Every month the "usb" drive with a full backup on it is stored off site at the Vermont State Public Records facility. Records are retained until data is reported as final then retained for 5 years, then destroyed

Instrument data for the organics and nutrient labs are backed up and electronically stored on a regular basis. Lachat and Dionex instrument data is backed up to a CD. Data is stored by month- day- year. The GC-MS is backed up

approximately every two months or more frequently during busy seasons, data is stored to CDs (8260, TO15). The HPLC is backed up on a Zip drive approximately every 6 months. Electronic backups are stored by the instruments. ICP/MS data is backed up yearly on a CD. Records are retained until data is reported as final then retained for 5 years, then destroyed

Records that are stored or generated by computers must be retained as a hard copy or have a write protected electronic copy. Records are retained until data is reported as final then retained for 5 years, then destroyed

Table 10.1 Record Storage Locations and Retention Times

Information	Storage Location	Type	Retention Time
Laboratory Standard Operating Procedures	Laboratory	Electronic Paper	5 years* 5 years
Vendor Supplied STD-Certificate of Analysis	Laboratory	Paper	5 years after expired or no longer in use
Notebooks	Laboratory	Paper	5 years after replaced or no longer in use
Instrument Raw Data	Laboratory	Electronic (disks, CDs)	5 years after data is reported*
	Laboratory	Paper	5 years after data is reported
LIMS Data	Separate State Building	DEC SQL Server Daily Tapes	Mon - Thurs nights starting at 11:55 pm Overwritten each week
	Locked Fire Proof Cabinet – (2nd Building)	Weekly Tapes	Friday nights starting at 11:55 pm. First Friday of each month, overwritten each month.
	Public Records Central Office (3rd Building)	Monthly Tapes	4th Friday night of each month starting at 11:55 pm 3rd, 6th, 9th and 12th months are kept for a year. All other monthly tapes are overwritten every 6 months.
		Yearly Tapes	Done on the last Friday of every year. These tapes are kept until obsolete (approx. 5 years).
Regulated D.W. Sample Receiving Forms	Laboratory	Paper	5 years after data is reported
Standard/Reagent Receiving Logs	See LIMS Data	See LIMS Data	5 years after data is reported

*Or until software is obsolete or information is no longer readable.

11.0 Quality Control Samples and Routines Used to Assess Accuracy and Precision

The purpose of this section is to define quality control procedures that are necessary to develop information which can be used to evaluate the quality of analytical data. Quality control (QC) terms are defined and an explanation of how, when and why QC samples are taken or analyzed is provided. This section is intended to be used as a guideline for laboratory users. Specific projects and methods may require additional or more frequent analysis of quality control samples due to such factors as difficult sample matrices, project requirements, critical measurements or enforcement actions.

11.1 Field Quality Control Samples

The results of quality control samples taken in the field reflect the precision and accuracy of the entire process, from sample collection through analyses. Below is a brief description of quality control samples laboratory users should collect when appropriate. Certain methods or projects may require additional QC samples not described here. Field quality control samples are logged into the Laboratory Data Management System by Laboratory users and assigned a sample ID number. Samples may be logged in as "blind" samples if desired. Synonymous terms are provided in parenthesis.

11.1.1 Blanks

11.1.1.1 Equipment Blanks

Equipment Blanks are a type of field blank used to determine if contamination has been introduced through contact with sampling equipment or to verify effectiveness of equipment cleaning procedures. Laboratory water free of analyte is transported to the site and processed through the sample collection device, preserved if necessary and returned to the lab for analysis. Laboratory water should not be stored for future use, a hold time of one week is recommended. Do not contaminate the carboys with field equipment. Do not use water from other sources or return water to the carboy. Equipment blanks should be processed whenever contamination is suspected, with each analytical batch or every 20 samples. Corrective action for contamination detected in equipment blanks is addressed by laboratory users evaluating data.

11.1.1.2 Field Blanks

Field Blanks are used to determine if analyte(s) of interest or chemical interferences are present in the field environment. This would include contamination from sample bottles, storage, transport and sample preparation. A field blank is usually laboratory deionized water that is transported to the sampling site, opened to the contaminated environment, and processed as a sample (filtration, preservation, etc.). One field blank should be submitted with

each analytical batch or every 20 samples or whenever contamination is suspected. Contamination detected in field blanks would need to be evaluated by both field and laboratory personnel.

11.1.1.3 Filter Blanks

Filter Blanks (Cartridge Blanks) are used to determine if method analytes or other interferences are introduced during the filtration or sampling process. Laboratory water is used to rinse the filter and filtration apparatus. Air filter blanks may also be submitted to determine if sample breakthrough has occurred. At least one filter blank should be processed with each sample batch or whenever contamination is suspected.

11.1.1.4 Trip Blanks

Trip Blanks are routinely used when sampling for volatile organic compounds. Volatile organic compounds are most susceptible to this type of contamination. The laboratory supplies samplers with a VOA vial containing acidified analyte free water. The vial is transported to the sampling site and returned to the lab without being opened. Sample contamination from penetration of the Teflon cap by halogenated solvents during transport or at the site can be detected with a trip blank. Trip blanks are logged into the data management system and are assigned a sample ID number.

11.1.2 Precision and Accuracy Checks

11.1.2.1 Field Duplicates

Field Duplicates (duplicate samples, replicate samples) are two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Results give a measure of the precision associated with sample collection, preservation and storage as well as with laboratory procedures. Field duplicate data provides the best measurement of precision from sample collection through analyses. Field duplicates should be taken on 5% of the sample volume. Duplicates are logged in as individual samples and can arrive at the laboratory as “blind” duplicates if the laboratory user desires. A field duplicate should not be confused with a split sample (Section 11.1.2.3).

11.1.2.2 Matrix Spikes

Matrix Spikes are the same as analytical matrix spikes (Section 11.2.4.3) except that spiking is done in the field. Spiking samples in the field is less reliable and more difficult than spiking in the laboratory and is not recommended.

Results from analytical matrix spikes are used to detect matrix interference and measure method accuracy. If a sample is spiked a percent recovery is provided on

the Final Laboratory Report. Spiked sample recovery results are useful to laboratory users. Method accuracy values provided by the laboratory in Table 5.1 may not be applicable to a particular sample or matrix that is being evaluated.

Grant requirements for most projects require a percentage of the samples being analyzed have a matrix spike added. Under these circumstances laboratory users may request matrix spike analysis and recovery results for a percentage of their samples or specific samples being submitted to the laboratory for analysis.

In order to provide laboratory users with matrix spike results for a specific sample or percentage of samples for a project, arrangements need to be made with the laboratory supervisor. The sample to be spiked is flagged with a "duplicate/spike" label by sample login personnel to alert the chemist who will be spiking the sample. The laboratory may need extra sample volume and or a split sample (phosphorus, TPH). If a split sample is needed the sample is logged into the Laboratory Data Management system as one sample (assigned one sample ID #). The sample container is labeled with a "duplicate/spike" label and the lab number of the sample that was split to alert chemists that the sample is to have matrix spike analysis. A percent recovery will be reported with the sample result on the final lab report. Matrix spikes are routinely analyzed at the laboratory. The sample is selected by the analyst if not requested by the laboratory user. The sample selected may not be from the batch of samples submitted by a client.

11.1.2.3 Split Samples

Split samples are aliquots of samples taken from the same sample container after thoroughly mixing or compositing the sample. They are analyzed independently and are used to document intra- or interlaboratory precision. Split samples may also be used by program personnel to request matrix spike analysis for tests requiring two separate samples.

11.1.2.4 Blind Samples

Blind samples are sample(s) submitted to the lab for analysis, the composition or origin of the sample is known to the submitter but unknown to the analyst. Blind samples can be a duplicate sample, blank, proficiency sample, or an interlab comparison sample.

11.2 Analytical Quality Control Samples, Solutions and Routines

Results of analytical quality control samples are used to estimate the precision and accuracy of data from sample preparation through analysis. Some of the data are reported with the associated sample result(s). In addition to the quality control samples in which results are released with the associated data there are several types of samples (solutions) that may be analyzed or procedures performed to verify the precision and accuracy of the entire system. Results may be used to verify calibration, identify reporting limitations or to help identify and if possible correct for instrument, method or sample interferences. Not all of these sample types will apply to every

analysis; some are instrument and method specific. Data acceptance criteria are method specified and if no specifications are provided they are based on historical data or internally established. Analytical quality control terms, the frequency of analysis, and how the information obtained from their analysis is used are described in this section. The underlined term is the term used within DEC Lab Standard Operating Procedures. Synonymous terms are used in different references and accreditation documents and are provided in parenthesis.

11.2.1 Negative Control (Blank) – Method Performance

The level of analyte of interest detected in the Method, Continuing Calibration, or Initial Calibration Blank is evaluated in relation to the sample result being reported within the batch. The general laboratory policy is to qualify any reported analytical results analyzed in the batch if the blank concentration is > ½ PQL and if 2 times the blank concentration is greater than the sample concentration. However, if the concentration of the target analyte in the blank is at or above the reporting limit AND is greater than $1/10^{th}$ of the amount measured in the sample a blank is determined to be contaminated and the source of contamination shall be investigated and measures taken to minimize or eliminate the problem. Method specified exceptions to this policy are identified below.

Samples associated with the blank contamination shall be evaluated as to the best corrective action for the samples.(e.g., reprocessing or data qualifying codes). In all cases the corrective action shall be documented. If data is reported and qualified all associated sample results must be flagged with the Sample Remark Code: "B- Reported value associated with a blank contamination". A sample or order comment may also be added to the LIMS describing the degree of contamination.

In some instances, increasing the reporting limit may be acceptable to a client. The Laboratory Supervisor must be consulted prior to increasing the reporting limit. If the limit is exceeded on a frequent basis and corrective actions are unable to resolve the problem the reporting limit will need to be re-evaluated.

Analyst/Supervisor discretion must be used when reporting results. If there are method or project data quality objectives or regulatory requirements for qualifying data associated with blank results those requirements must be followed if the requirements are more stringent. The following methods or situations are exceptions to the above policy.

<u>METALS</u>:
In the absence of project specific data quality objectives the method blank is considered acceptable if the concentration is less than 10% of any reported sample concentration. If the method blank exceeds the criteria but sample results are below the limit of quantitation then the sample data may be used despite the contamination of the method blank without qualification. If the method blank is not acceptable it should be rerun once. If the method blank is unacceptable sample results that are greater then the lower limit of quantitation can be reported

but must be flagged if the method blank concentration is >10% of the sample concentration. The sample remark code "B- Reported value is associated with a lab blank contamination" is used.

AIR METHODS:
Method TO15 (volatiles): 0.1 ppbv or MDL, whichever is greater.
Method TO11 (carbonyls): 0.15, 0.1 and 0.3 µg/cartridge for formaldehyde, acetaldehyde, and acetone respectively. All other compounds 0.1 µg/cartridge.
Method IO 3.5 (metals): ≤5 X MDL

INORGANICS:
Total Nitrogen (TN): Method Blanks are used to correct for known contamination from reagents and the preparation and processing of samples. Results are blank corrected by subtracting the Method Blank average from the analytical run from each analytical result.

11.2.1.1 Initial Calibration Blanks – ICB

Initial Calibration Blanks are aqueous solutions prepared and diluted with the same volume of chemical reagents and solvents used in the preparation of the primary calibration standards. They may be used to give a null reading for the instrument response when running a calibration curve or to establish instrument background. The initial calibration blank does not assess for possible contamination during the preparation and processing steps. The ICB is analyzed as a sample at the beginning of the analytical run.

11.2.1.2 Continuing Calibration Blank – CCB

Continuing Calibration Blank is the ICB solution that is reanalyzed at a regular interval throughout an analytical run to assess baseline drift.

11.2.1.3 Method Blank

Method Blank (Laboratory Reagent Blank, Preparation Blank), is a volume of deionized laboratory reagent water carried through the entire analytical procedure including all preparation, filtration and processing steps carried out by the analyst. The Method Blank contains the same reagent(s) as the samples. Analysis of a method blank verifies that interferences from contaminants in solvent, reagents, glassware and other sample processing devices are quantified. A method blank is analyzed at a minimum of 1 per preparation batch (up to 20 samples) for methods that have a preparation procedure.

11.2.2 Positive Controls – Method Performance

11.2.2.1 Laboratory Control Samples – LCS

Laboratory Control Samples – LCS (Blank Spike, Laboratory Fortified Blanks) are prepared by adding known quantities of the method analyte(s) to a volume of reagent water. Laboratory Control Samples must be processed at a minimum of 1 per preparation batch (up to 20 samples). The LCS solution is the same solution used for matrix spikes. The LCS must be processed exactly like samples within the analytical batch. The concentration is typically mid-range (LCS-mid) at least one LCS low is also analyzed to verify the limit of quantitation (see 11.2.2.2). LCS results are used to evaluate the total analytical process including all preparation and analysis steps. LCS results are also used to evaluate matrix spike recovery results since the solution used to spike the LCS is the same solution used for sample matrix spikes.

The results of LCS are reported as a percent recovery and are tracked in the LIMS. LCS control limits are those established in the referenced method. If there are no established criteria, the lab determines internal criteria based on historical data. If an LCS recovery is outside the control limit the LCS solution may be reanalyzed. If the reanalysis of the solution is acceptable a note is made on the bench sheet and results are accepted. Any samples associated with an unacceptable LCS must be reprocessed and re-analyzed or the associated sample results and LCS results are to be reported with a data qualifier.

For multi-parameter methods, the components to be spiked and the acceptance criteria shall be as specified by the referenced test method or other regulatory requirement. If acceptance criteria are not specified and a large number of analytes are in the LCS, Standard Operating Procedures may allow for a number of parameters to marginally exceed limits. If spiking components are not specified TNI requires the following:

- For those components that interfere with an accurate assessment the spike should be chosen that represents the chemistries and elution patterns of the components to be reported.

- For those test methods that have extremely long lists of analytes, a representative number may be chosen and should represent all analytes reported. The following criteria are used to determine the number of analytes to be spiked. The laboratory should spike all target analytes over a two-year period if available.

  For a method that includes 1-10 components spike all components.
  For a method that includes 11-20 targets, spike at least 10 or 80%, whichever is greater.
  For methods with more than 20 targets, spike at least 16 components.

11.2.2.2 Low Level Laboratory Control Standards (LCS Low)

Low Level Laboratory Control Standard (Limit of Quantitation Verification – LOQ) are prepared and processed exactly like an LCS (Section 11.2.2.1). The

concentration of the LCS Low is at or near the laboratory reporting limit (PQL). One LCS Low is processed with each analytical run.

Results are used to evaluate the performance of a method at the reporting limit. Results are reported in the LIMS and a percent recovery is calculated. The analysis of the LCS Low satisfies the lab's requirement of verifying the limit of quantitation (LOQ). The analysis of an LCS Low was established as policy in 2009. The lab will establish acceptance criteria using historical data. Variability at the low end of the curve is greater than the mid-range and limits are expected to be wider than those established for the mid-level LCS.

11.2.2.3 Quality Control Sample (QCS)

Quality Control Sample – (Certified Reference Material CRM) Standard Reference Material SRM) can be either an uncontaminated sample matrix, (i.e. fish, soil, ash) spiked with known amounts of analytes or a contaminated sample matrix. The QCS is a NIST certified standard purchased to establish intra-laboratory or analyst specific precision and bias or to assess the performance of the measurement system. QCS results are tracked in the LIMS.

11.2.3 Standards – Method Calibration

11.2.3.1 Primary Calibration Standards

Primary Calibration Standards (Primary Standard, Calibration Standard) are prepared from dilutions of a NIST traceable stock standard solution or are prepared in-house from reagent grade materials. The standards are used to calibrate the instrument response with respect to analyte concentration.

11.2.3.2 Initial Calibration Verification Standard – ICV

Initial Calibration Verification Standard – ICV (Second Source Standard, Quality Control Check Sample, and Initial Performance Check-IPC) is a certified reference standard from a source different then the primary calibration standard. When available they are processed the same as the primary calibration standard and are an independent check on the primary standard used to calibrate the instrument.

ICVs are analyzed immediately following calibration and determine if sample analysis can proceed. The concentration of the ICV is approximately the mid-level of the calibration range. If acceptance limits are not method specified they are established in-house. If the first analysis does not produce an acceptable result the sample may be reanalyzed once. If the second attempt does not generate an acceptable result the analysis of samples may not proceed. The source of the error needs to be determined and corrective actions taken.

Under unusual circumstances results may be reported without a passing ICV (i.e.

ICV solution has degraded and the fresh solution is unavailable and all other QC is acceptable). The Laboratory Supervisor must be consulted and associated data will likely be qualified. The client may be contacted prior to releasing data.

The second source standard result generated at the beginning of the run is calculated as a percent recovery and tracked in the LIMS.

11.2.3.3 Continuing Calibration Verification Standard – CCV

Continuing Calibration Verification Standard – CCV (Calibration Check Standards, Same Source Standard, Calibration Check Compounds, Calibration Verification Check – CVC, or Continuing Calibration Check Standards – CCC) is a primary calibration standard(s) that is reanalyzed with test samples to verify continued calibration of the analytical system.

The concentration of the CCV must be varied within an analytical run. For most analyses a mid-level Continued Calibration Verification Standard (CCV-Mid) is analyzed at the beginning and end of the analytical run and after every 10 samples for large analytical runs. The laboratory also requires that the reporting limit of a method is verified by analyzing either a low level continuing calibration verification standard (CCV Low) or Laboratory Control Sample (LCS-Low), which ever is applicable, within each analytical run (see Limit of Quantitation, Section 14.4.4). The standard must be at or near the concentration of the low standard (PQL). Acceptance criteria for the CCV Low will be wider than the CCV-Mid criteria. An unacceptable bias at the low end of the calibration curve will require corrective action or an increase in the reporting limit (PQL).

The CCV is expressed as a percent recovery. Reported results should be bracketed by acceptable CCV-Mid level standards. If an internal standard is used, only one verification needs to be performed at the beginning of the analytical batch or every 12 hours, whichever is more frequent (i.e. Method 8260). (See 2003 NELAC Standard Section 5.5.5.10c). Acceptance criteria and corrective actions required if criteria are not met must be documented in method Standard Operating Procedures. If limits can't be met affected samples can be reanalyzed once prior to taking corrective actions.

If there is a method specified acceptance criterion it must be used. If no criterion is specified the Laboratory establishes one. Under certain circumstances results may be reported without a passing CCV. Sample results not bracketed by a passing CCV are flagged with an "E- Estimated Value" or another appropriate Sample Remark Code. Analyst discretion is needed when determining if data will be flagged or corrective actions taken and samples reanalyzed.

For multi component methods that allow a periodic check on the initial calibration curve rather than a daily calibration, the calibration check standards are groups of specific representative compounds. They are analyzed every 12 hours.

The number of compounds analyzed is based on the number of target analytes on the list.

- 1-10 targets, spike all components.
- 11-20 targets, spike at least 10 or 80% whichever is greater.
- >20 targets, spike at least 16 components.

Note: The laboratory is required to analyze all target compounds over a two-year period.

11.2.3.4 Internal Standards

Internal Standards (IS) are used for some organic methods and ICP/MS technology. The standards are added to every standard, blank, matrix spike, matrix spike duplicate and sample extract at a known concentration prior to analysis. Internal standards are used as the basis for the quantitation of the target compounds for several organic methods.

For ICP/MS the internal standard solution is used to monitor the analysis for matrix effects and correct for instrument drift throughout the analysis. When IS criteria are not met the sample is diluted and reanalyzed until IS recoveries are within acceptance limits. For parameters associated with failed IS recoveries the reporting limit must be increased by the dilution factor. Alternatively results can be flagged and an Order comment describing the potential inaccuracy in the reported results can be added to the Final Report.

11.2.4 Precision and Accuracy Checks – Sample Specific Controls

11.2.4.1 Analytical Sample Duplicate

Analytical Sample Duplicate (Duplicate, Lab Duplicates) are two aliquots taken from the same sample container that are processed and analyzed separately. Results are used to measure analytical precision from sample preparation through analysis for a given matrix. A minimum of 5% of all samples are analyzed in duplicate when sufficient sample volume is provided

Some parameters require a separate sample volume in order to perform a "duplicate" analysis. For those tests the first volume is either compromised during the initial analysis (i.e. volatiles) or the entire sample must be processed and can not be subdivided (i.e. total phosphorus, method 8015). A carefully subdivided field split sample is required. Table 6.1 identifies parameters that require a split sample.

When a sample is analyzed in duplicate the first result recorded appears in the final laboratory report result column. The second result and the relative percent difference (RPD) of the duplicate values are reported in the QC results section of

the report. The RPD calculation can be found in Section 14.1 of this manual. Historical data from the analysis of laboratory duplicates are used by the laboratory to establish precision control limits. Laboratory limits can not be wider than method required acceptance limits unless data is flagged

If the sample duplicate Relative Percent Difference (RPD) is outside the laboratory control limit an 'OL – outside limit' flag is applied.

When control limits are exceeded the analyst must take further action to assure that a correctable error was not the cause of the irregularity. The analyst should evaluate possible human and analytical reasons for the excedence. The evaluation may include: a review of the chromatography, sample cup placement, instrument operation, sample matrix, analyte concentration and other potential causes for the excedence.
The analyst is allowed to repeat analysis once. If after re-analysis the RPD falls within the established limit the new result(s) can be reported as long as there is clear documentation and traceability of the reported result. If the RPD is still outside limits and if all other QC within the run are acceptable the analyst can report the initial result(s) if properly qualified. If there is evidence that the analytical system is not in control analysis must stop and results must not be reported. In some situations reanalysis is impossible (insufficient sample volume) or impractical (hold time has been exceeded or there is a known documented interference that can not be corrected for). If the analyst suspects that a processing error occurred that impacts all of the samples analyzed then the entire analytical batch must be reprocessed and reanalyzed.

If the sample matrix is thought to be the cause of the imprecision then an order comment should be added to the report so that all results of similar composition are flagged.

11.2.4.2 Instrument Duplicates

Instrument Duplicates are two aliquots taken from the same extract or digestate and analyzed in duplicate. Results are used to measure instrument precision only. The average value of instrument duplicates may be reported, however method precision may not be calculated using instrument duplicates for methods requiring predigestion, extraction or any other sample preparation steps.

11.2.4.3 Matrix Spikes – MS

Matrix Spikes – MS (Laboratory Fortified Sample Matrix) are prepared by adding a predetermined quantity of stock solution of the analyte(s) being measured to a sample prior to sample extraction/digestion and analysis. The stock solution must be the same solution used to prepare the LCS. The concentration of the spike should be at the regulatory standard level or spiked at a level that will result in a final concentration that is approximately 1.5 times the unspiked concentration.

The analyst must anticipate if possible, any dilutions that will be needed prior to analysis and spike the sample at a higher concentration. The volume of the spiking solution must be less than 5% of the sample volume being spiked. A portion of the unspiked and the spiked sample are analyzed and a percent recovery is calculated (Section 14.2). Recovery data provides a measure of accuracy for the method used in a given matrix.

Recovery results verify the presence or absence of matrix effects and are particularly important when analyzing complex matrices (soil, sludge, sediment or samples with interferences). Five percent of all samples received at the lab are spiked when sufficient sample volume is provided or at a rate specified by the test method or project plan. If a sample is spiked the calculated percent recovery is reported on Final Laboratory Reports. Samples of some methods cannot be spiked (i.e., chlorophyll, dissolved oxygen, turbidity). Samples to be spiked are selected by the analyst unless they are pre-selected by laboratory users (see Section 11.1.2.2).

Acceptance limits for matrix spikes analyzed at the lab will vary depending on the analysis, matrix and sample concentration level. Acceptance limits are either method specified or established from historical laboratory results. The narrower limits must be used. If recovery data is unacceptable, and the laboratory control sample (LCS) is within acceptance limits a matrix interference may be the cause of the irregularity.

Sample results associated with a Matrix Spike Recovery (MS) outside the laboratory control limit(s) must be flagged. If a result is outside the established control limit (OL)and the LCS is acceptable the analyst must:

- Flag the QC result that is OL.
- Flag associated sample results with an appropriate Sample Remark Code or provide a Sample or Order Comment if further qualification is needed or warranted.
- Notify the Laboratory Supervisor if the analyst is unsure whether results should be reported.

When control limits are exceeded beyond ±10 the analyst must take further action to assure that a correctable error was not the cause of the irregularity. The analyst must re-prepare and reanalyze the sample and MS (i.e. if limits are 80-120%, reprep and analysis is required if outside 70-130%).

The analyst is allowed to repeat analysis once. If after re-analysis the result(s) fall within the established limits the new result(s) can be reported as long as there is clear documentation and traceability of the reported result. If the MS result is still outside limits and all other QC within the run are acceptable the analyst can report the initial result(s) if properly qualified. If there is evidence that the analytical system is not in control analysis must stop and results must not be reported. In some situations reanalysis is impossible (insufficient sample volume) or impractical (hold time has been exceeded or there is a known documented

interference that can not be corrected for).

If an interference is suspected the analyst may spike a series of dilutions to verify and eliminate or reduce the effect of the interference. In some instances analysts are able to eliminate the interference and report uncompromised data. However, if the required dilution is large and the original sample is no longer represented in the diluted sample or the analyte of interest is diluted below the PQL results may not be reported or reported as <PQL unless properly qualified. The client is responsible for determining the usability of flagged Matrix Spike sample results.

11.2.4.4 Matrix Spike Duplicate – MSD

Method precision can also be calculated from matrix spike duplicates. Matrix spike duplicates are used to estimate method precision for analytes that are frequently found below the practical quantitation limit. A second aliquot of the sample is treated like the original matrix spike sample. The relative percent difference (RPD) of the matrix spike and the matrix spike duplicate is calculated and is used to assess analytical precision. Final laboratory reports indicate when RPD values are calculated from matrix spike duplicates.

11.2.4.5 Surrogates

Surrogates are organic compounds, which are not found in environmental samples, but have similar chemical structures, and extraction and/or chromatography properties. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicate and laboratory control samples) prior to analysis by GC or GC/MS. Percent recoveries are calculated for each surrogate. Surrogate compounds and their acceptable recovery ranges are specified in analytical methods and are listed in Standard Operating Procedures (SOPs) for organic methods. The Laboratory tracks surrogate recovery results and the historical data is used to monitor systems and establish warning limits that are narrower than the method specified control limits. Recovery data is reported with every sample result. When a recovery value is not within acceptance limits calculations and surrogate solutions are rechecked. Samples or extracts may be reanalyzed. If results are still not within suggested limits a flag “S-surrogate recovery outside acceptance limits” must be added next to the surrogate result that exceeds a criterion.

11.2.5 Limits

11.2.5.1 Method Detection Limits (MDL)

Method Detection Limit is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from repeated analysis of low level samples in a given matrix containing the analyte at a predetermined level. MDLs are determined annually for most analytes and matrices. The process and formula used to generate MDLs are described in Section 14.4.

11.2.5.2 Practical Quantitation Limit (PQL)

Practical Quantitation Limit (PQL) (Reporting Limit, Limit of Quantitation - LOQ) is the lowest level that can be reliably achieved during routine laboratory operating conditions. The PQL is approximately two to ten times the calculated MDL. PQLs are a preferred reporting limit because MDL values will change each
time they are calculated even though the analytical procedures, instruments and sample matrices are the same. Using the PQL as a reporting limit allows laboratory clients to be assured that all reported results are bracketed by standards that meet method acceptance criteria.

In the organics analytical center a N.D. (not detected) appears on final laboratory report forms rather than <PQL value. However, if a compound is detected at a level that is less than the PQL and the value is no less than one half the PQL; a <"PQL" (of the compound in question) is reported rather than a N.D.

For organic results the Laboratory Reporting Limit (PQL) must increase if sample dilution is required. The increase in the PQL will be equivalent to the dilution factor. For multi parameter methods the analyst must make an effort to report results from the least dilute analysis for each parameter. If sample results are reported from two analysis, then the PQL is increased for the parameters reported from the diluted sample. If for some reason it is impractical to increase the PQL at final report time, another form of qualification must be implemented.

For inorganic analysis the PQL must be increased if sample dilution is required to eliminate interference. The increase in the PQL is equivalent to the dilution factor.

11.2.5.3 Instrument Detection Limit (IDL) (ICP-MS only)

Estimated by calculating the average of the standard deviation of three runs on three non-consecutive days from the analysis of a reagent blank solution (which is equivalent to a calibration blank for waters) with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample. IDLs should be determined every three months.

11.2.5.4 Preparation Batch

Preparation Batch is composed of one to twenty environmental samples of the same matrix that are prepared and analyzed together with the same processes, personnel, and reagent(s). The maximum time between the start of processing of the first and last sample in a preparation batch is 24 hours.

11.2.5.5 Analytical Batch

Analytical batch is defined as a group of samples (extracts, digestates or environmental samples) that are analyzed together with the same processes, personnel, and reagents and having a defined set of quality control samples. Several preparation batches can be analyzed together in an analytical batch but each preparation batch must have associated QC data.

11.2.6 Instrument Checks

11.2.6.1 Tuning Solutions

Tuning Solutions are used to verify that the resolution and mass calibration of the instrument are within required specifications prior to calibration and sample analysis (GC/MS) and to set the operating parameters of the instrument for the ICP/MS.

11.2.6.2 Interference Check Solutions (ICS)Interference Check Solutions (ICS) contain known concentrations of interfering elements. They are analyzed prior to samples to demonstrate that correction equations are adequate (ICP/MS).

12.0 Audits and Demonstrations of Capability

System and performance audits are used to assess the overall effectiveness of the DEC Laboratory's quality assurance program. Performance audits may be conducted by the DEC Laboratory Quality Assurance Office (internal) or by various government agencies (external). Demonstration of capability must be made prior to using a test method or if there is a change of equipment type, personnel or test method.

12.1 System Audits

A system audit is a qualitative evaluation of all components of a measurement system. System audits can be conducted by external auditing authorities (external audit) or can be conducted in-house (internal audit).

The DEC Laboratory is accredited by the NELAC Institute (TNI). A TNI accrediting authority (New Hampshire Environmental Laboratory Accreditation Program-NHELAP) conducts an on-site system audit of the DEC Laboratory every two years. A U.S. EPA Region I Office of Environmental Measurement and Evaluation representative is on the audit team. EPA Region I accepts the accreditation status of NH ELAP. Continued accreditation for individual parameters or methods is dependent on successful analysis of semi-annual proficiency samples supplied by a TNI approved proficiency provider. The audit team evaluates Laboratory QC procedures, technical staff, analytical activities and the Laboratory's quality assurance program. The next on-site evaluation will be conducted in May of 2015.

External system audits are also periodically conducted by the USGS; RTI and the USEPA Region 1 Office of Research and Development, Ecosystem Research Division. The USEPA Ecosystem Research Division audits the Lab as a result of our involvement in the analysis of mercury. Battelle, under contract to EPA, performed a technical audit of Laboratory air methods in July 2004, and in May of 2007. RTL International under contract to EPA performed a technical audit of the Laboratory's air method TO11 in August 2010.

Internal System Audits are a tool to: verify analyst compliance with the laboratories quality policies; to address any on going quality issues; and to highlight technical, equipment or management support needed within the analytical center being audited. It is the responsibility of the Laboratory's QA Officer to plan and organize internal audits within each of the laboratory's analytical centers. Internal audits of each analytical center are performed annually. Audits are conducted by qualified personnel that are independent of the activity being audited. Under certain circumstances a qualified chemist from another organization assists in the audit.

Internal audits generally review all aspects of sample analyses from sample preparation to data reporting and review. In some instances the analyst is required to analyze a sample(s) of unknown concentration(s) while the auditor(s) observe. All notebooks and records are checked for traceability. SOPs are reviewed prior to the audit to assure written protocols are being followed. Checklists from external auditing organizations are often used. Previous audit reports are reviewed prior to an internal audit to assure that previously recommended corrective actions have been implemented. An Audit Report summarizing the method(s) reviewed and findings

and recommendations is distributed to management and analysts audited. The analysts being audited have an opportunity to add to the Audit Report any comments or recommendations to management that would assist in improving the overall function of the section and the quality of data being generated. If during the course of an audit or at any other time a significant departure from the QA Plan policies, method SOP, requirements or TNI standards are revealed the findings will be documented and corrective actions will be required. Discovery of potential issues shall be handled in a confidential manner until such time as a follow up evaluation, full investigation, or other appropriate action have been completed and the issues clarified. The need to contact customers will depend on the severity of the departure and the effect the departure had on released data. The Laboratory Supervisor must notify clients in writing if audit findings cast doubt on Laboratory results. Follow-up audit activities shall verify and record the implementation and effectiveness of the correction action taken.

12.2 Performance Audits

Performance audits determine quantitatively the accuracy of analytical data. This is primarily accomplished by means of interlaboratory performance evaluations. Laboratory staff analyze reference materials and are rated on their performance. Each proficiency provider has a unique rating system and acceptance criteria and vary in difficulty.

Proficiency samples must be handled in the same manner as real environmental samples. This includes using the same staff, methods, procedures, frequency of analysis, reporting protocol, equipment and facility used for routine analysis. The Laboratory maintains records of the analysis of all PTs for at least 5 years.

Proficiency audit results are reviewed by the Laboratory Quality Assurance Officer and distributed to the Laboratory Supervisor, laboratory staff and to laboratory users when requested. Reports for Water Supply (WS) and Water Pollution (WP) Proficiency Audits must be sent to the Laboratory's TNI accrediting authority. Accreditation status is dependent on successful analysis of these samples.

A Quality Assurance Irregularity Report (Figure 15.1) will be issued to the lead analyst if criteria are not met. An "unacceptable" rating for the Water Supply (WS) and Water Pollution (WP) proficiency audits would require the completion of an Irregularity Report. In order to remain TNI certified for an analyte the Laboratory must participate in semi-annual evaluations and must obtain acceptable ratings on two of the last three studies.

The USGS Study reports results as a % difference from the Most Probable Value (MPV). The QA Office issues an Irregularity Report if the % difference is >20% of the median.

The National Water Research Institute Study (NWRI) rates results from ten separate samples for each analyte. Individual results are rated either: action low, warning low, satisfactory, warning high, or action high. Any of the following scenarios would require the analyst to complete an Irregularity Report:

- one or more action low or action high result
- three or more of the ten samples flagged (warning low, warning high).
- Systematic Bias – percent slope greater than the absolute value of 5 and parameter flagged "Biased High" or "Biased Low" without an asterisk (asterisk indicates that the bias is considered minor, yet worthy of evaluation).

Eastern Research Group proficiency audit results for organics in air are rated against method specified acceptance criteria. If criteria are not met for a compound, an Irregularity Report is issued. The National Air Toxics Trends Stations (NATTS) Audit uses ±20% and ±25% of the true value as warning and acceptance limits.

Irregularity Reports are reviewed by the Laboratory Supervisor and Quality Assurance Officer and kept on file in a central location. If Irregularity Reports are not returned to the Quality Assurance Officer by the required due date the Laboratory Supervisor is notified.

Unacceptable results or trends from proficiency evaluations may necessitate an internal audit of the method in question. The audit is initiated by the Laboratory Quality Assurance Officer who may submit blind check samples for analysis.

Performance evaluations in which the DEC Laboratory participate in are listed below.

12.2.1 Water Pollution Study (WP Series) - semi-annual evaluation. Results are submitted for both methods of analysis when the laboratory reports results by more than one method.

- Trace Metals (aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, mercury, manganese, molybdenum, nickel, selenium, vanadium, zinc, silver, strontium, thallium)
- Minerals (spec. cond., total dissolved solids, total hardness, calcium, magnesium, total alkalinity, chloride, sulfate, sodium, potassium, fluoride)
- Nutrients (ammonia as nitrogen, nitrate as nitrogen, total Kjeldahl-nitrogen, total phosphorus, total nitrate and nitrite)
- Demands (COD, 5-day BOD)
- Volatile Halocarbons
- Volatile Aromatics
- Miscellaneous Parameters (total suspended solids, volatile solids, total residual chlorine, pH, turbidity, nitrite, silica, Gasoline Range Organics, Diesel Range Organics)

12.2.2 Water Supply Performance Evaluation (WS Series) – semi-annual evaluation

- At this time the DEC is not performing drinking water analyses.

12.2.3 U.S. Geological Survey Analytical Evaluation Program - semi-annual evaluation

- Nutrients (nitrate/nitrite as nitrogen, phosphorus, ammonia, nitrate, total nitrogen, silica).
- Trace Constituents (aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, sodium, selenium, strontium, silica, silver, thallium, vanadium, uranium, zinc)
- Major Constituents (chloride, sulfate, specific conductance, silica, alkalinity, pH, total phosphorus, calcium, potassium, magnesium, sodium)
- Precipitation (conductivity, pH, sulfate, calcium, magnesium, potassium, sodium, total phosphorus)

12.2.4 National Water Research Institute Evaluation (NWRI) - 2/year

- Acid Rain Parameters (color, spec. conductance, pH, gran-alkalinity, sodium, magnesium, potassium, aluminum, sulfate, chloride, calcium, nitrate-nitrogen, hardness).

12.2.5 National Air Toxics Trends Stations (NATTS)

- metals – Teflon air filters (6 parameters) – when available
- Volatile organic compounds – air (14 compounds) – when available
- Carbonyl compounds- air (3 compounds) – when available

12.2.6 Air Proficiencies – 0-2/year (per client request)

- carbonyl compounds - air (5 compounds) - ERG
- volatile organic compounds -air (60 compounds) - ERG
- metals – air filter strip (16 parameters) – Wibby

12.2.7 Underground Storage Tanks (UST)

- Gasoline Range Organics (soil)
- Diesel Range Organics (soil)

12.3 Demonstration of Capability

12.3.1 Initial Demonstration of Capability (DOC)

12.3.1.1 New Method or Technology DOC

Instruments purchased and methods developed after 12/2000 should have an Initial Demonstration of capability file. The demonstration of capability must be made prior to using any test method or any time there is a change of instrument type or test method. If there are method specified criteria they must be followed. When the method does not specify a procedure, the following steps should be documented when applicable:

- The technical director of each analytical center shall participate in vendor provided training courses when new technology is employed.
- Demonstration of linearity.
- Method Detection Limit study.
- Accuracy - typically demonstrated by analysis of an internal blind NIST traceable standard at one or more concentrations.
- Precision - repeated analysis of a known sample four times. The following TNI protocol outlined in 12.3.1.2 of this document must be used as of 6-2003 if required by mandatory test method or regulation.

All demonstrations shall be documented through the use of the TNI "Demonstration of Capability Certification Statement" form.

12.3.1.2 Precision and Accuracy Assessment (Source 2003 TNI Standard, Chapter 5 –Appendix C Demonstration of Capability

- A quality control sample shall be obtained from an outside source. If not available, the QC sample may be prepared by the Laboratory using stock standards that are prepared independently from those used in instrument calibration.
- The analyte(s) shall be diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified, or if unspecified, to a concentration approximately 10 times the method-stated or Laboratory-calculated method detection limit.
- At least four aliquots shall be prepared and analyzed according to the test method either concurrently or over a period of days.
- Using all of the results, calculate the mean recovery (X) in the appropriate reporting units (such as µg/l) and the standard deviations of the population sample (n-1) 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 must assess performance against established and documented criteria.
- Compare the information from above to the corresponding acceptance criteria for precision and accuracy in the test

method (if applicable) or in Laboratory-generated acceptance criteria (if there are not established mandatory criteria). If all parameters meet the acceptance criteria, the analysis of actual samples may begin. If any one of the parameters do not meet the acceptance criteria, the performance is unacceptable for that parameter.

- When one or more of the tested parameters fail the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for all parameters of interest.

Repeated failure, confirms a general problem with the measurement system that must be corrected.

For some methods NIST traceable standards are not available. In these instances the Laboratory purchases second source standards from TNI accredited vendors. For air method this Laboratory purchases blind proficiencies from a private lab. Split sample analysis between the DEC Laboratory and a reputable Laboratory is also utilized as a mechanism to validate a method using real world samples.

12.3.1.3 New Analyst Demonstration of Capability (DOC)

A demonstration of ability is required prior to a new analyst reporting results for an established method that has an initial method/instrument DOC on file but has not previously been performed by the analyst. The analyst must review all referenced methods, pertinent instrument manuals, and current method SOP. The analyst must observe the current analyst through all aspects of the procedure (sample preparation through reporting). The new analyst must also be observed processing QC samples to assess accuracy and precision by the primary analyst. Requirements vary depending on the complexity of the equipment or procedure to be performed. Accepted materials for this document shall consist of one of the following at least once per year. (A) Acceptable performance of blind sample (one of the semi-annual Performance Evaluation Samples), (B) Initial measurement system evaluation or another demonstration of capability (C) At least 4 consecutive laboratory control samples with

acceptable levels of precisions of accuracy (LCS or ICV), (D) Authentic samples with results statistically indistinguishable from those obtained by another trained analyst, i.e. dissolved oxygen sample / duplicate.

12.3.1.4 Analyst files are to contain training documentation.

12.3.2 Continued Demonstration of Proficiency

Analyst must demonstrate continued proficiency at least once a year for tests they are reporting results for. Analyst training files must contain a copy of a proficiency sample result that is rated acceptable (policy initiated 6-2003).

13.0 Preventative Maintenance

Preventative maintenance is scheduled for most analytical equipment within the DEC Laboratory to minimize poor performance, instrument down time and subsequent "interruption" of analyses. Major analytical equipment is maintained under service contract, other instruments are maintained by a qualified analytical instrument repair service. Preventative maintenance schedules are listed in Table 13.1

Routine maintenance is performed on all analytical equipment by qualified Laboratory personnel. When it is practical, an inventory of critical replacement parts and spare parts needed for routine maintenance is maintained for each instrument. Logbooks are kept for each major instrument to document instrument problems, repairs and routine maintenance.

Table 13.1 Laboratory Instrument Maintenance Schedule

Instrument – Manufacturer – Model	Maintenance Contractor*	Preventative Maintenance Schedule – Year in Service
INORGANIC		
pH/Millivolt Meter, Orion plus	QC Services	1/year – Year In Service 2007
Non-Ratio Turbidity meter, HF Scientific Micro 100	QC Services	1/year – Year In Service 2004
Spectrophotometer, Genysis – Thermo Spectronic 10	QC Services	1/year – Year In Service 2002
Dissolved Oxygen Meter, YSI Model 5100	QC Services	1/year – Year In Service 2003
Fluorometer, Turner Model TD-700	QC Services	As Needed – Year In Service 2001
COD Reactor, Hach Model 45600 (2)	QC Services	1/year – Year In Service 1990/2002
Centrifuge, International Equipment – EXD	QC Services	As Needed – Year In Service 1973
Conductance Meter, YSI Model 3200	QC Services	1/year – Year In Service 1999
Oven Precision – (2)	QC Services	1/year – Year In Service 1997/2005
Chlorine Pocket Colorimeter – Hach	QC Services	Year In Service 1997
Micro Distillation System – Lachat	—	Year In Service 1996
Auto Analyzer Systems, Lachat – QC 8000	Lachat	As Needed – Year In Service 1996
Auto Analyzer System, Lachat QuickChem FIA 8000 Series	Lachat	As Needed – Year In Service 2004
Ion Chromatograph, Dionex DX 320	Dionex	1/year – Year In Service 2000
Sonification Bath, Branson 2510	—	Year In Service 2006
METALS		
ICP/MS Thermo-Elemental X Series	Thermo-Elemental	1/year – Year In Service 2003
Automated Mercury Analyzer, Perkin-Elmer FIMS100	Perkin-Elmer	As Needed – Year In Service 2001
Microwave Digestion Furnace – CEM MDS 2100	CEM	As Needed – Year In Service 1993
Hot Block Digestors- Environmental Express (2)	—	Year In Service 2000/2003
Oven – Fisher Scientific, Model 625	—	Year in Service 2008
Sonicator – Branson 2510	—	Year in Service 2005
Water Bath - Precision		Year In Service 2001
ICP Spectrophotometer – ICAP 6000 and ASX-520 Auto Sampler	Thermo Scientific	Year In Service 2009
MICROBIOLOGY		
Autoclave, Getinge 122LS	Getinge	4/year – Year In Service 2001
Waterbath, Precision Model 260	—	Year In Service 2004
Air Incubators, Fisher Scientific Model 650F (2)	—	Year In Service 2001/2004

Instrument – Manufacturer – Model	Maintenance Contractor*	Preventative Maintenance Schedule – Year in Service
Quanti Tray Sealer, IDEXX Model 2X	---—	Year In Service 2000
ORGANICS		
GC/MS system, HP 6890/5973 (2)	HSS Hardware and Software Systems	1/year – Year In Service 1999/2005
GC System (Volatiles), HP 5890 (PID/FID Detectors)	HSS - Hardware and Software Services	As Needed – Year In Service 1994
TurboVap Evaporator, Zymark 500 (1), Caliper (1)	—	Year In Service 1994/2005
HPLC, Waters 2487	Waters	1/year – Year In Service 1999
Cryogenic Concentrator, Entech 7100	Entech	As Needed – Year In Service 2008
Canister Cleaner, Entech 3100 A	Entech	As Needed – Year In Service 2005
Gas Mixing System, Model 4600A	Entech	As Needed – Year In Service 2006
Aadco Pure Air Generator, 737	—	Year In Service 1999
Autosampler, Entech 7016CA	Entech	As Needed – Year In Service 2001
GC System(TPH) HP6890 (FID/ ECD Detectors)	HSS- Hardware and Software Services	As Needed – Year In Service 2003
Tekmar Purge and Trap (3100) with Archon Autosampler	Varian	As Needed – Year In Service 2003
Tekmar Purge and Trap (3000) and Autosampler (Aquatec 70)	Tekmar	As Needed – Year In Service 2006
ANALYTICAL BALANCES		
Balance, Mettler ????	QC Services	1/year – Year In Service 199?
Balance, Mettler AE200	QC Services	1/year – Year In Service 1987
Balance, Mettler AT400	QC Services	Out of service
Balance, Mettler PM400	QC Services	1/year – Year In Service 1987
Balance, OHAUS B 1500D	QC Services	1/year – Year In Service 1983
MISCELLANEOUS		
Exhaust Hoods (3)	UVM	As Needed – Year In Service 1991
Microzone Hoods (2)	ENV. Service	As Needed – Year In Service 2001
Refrigeration Units (12)	—	Year In Service - Various Years
Glassware Washer	Steris	4/year – Year In Service 1991
D. I. Water System	Siemens	2/year – Year In Service 2003

Instrument – Manufacturer – Model	Maintenance Contractor*	Preventative Maintenance Schedule – Year in Service
Electronic Pipettes (14)	Rainin	1/year – Year In Service - Various Years
Manual Pipettes (3)	Rainin/Eppendorf	1/year – Year In Service - Various Years
Weight Set: Rice Lake 13 piece set	—	Internally 1/year.
ERTCO Thermometer	ERTCO	Every 5 years or as needed

[a] QC Services is ISO 9002 registered, ISO 17025 compliant.
[b] For older instruments, year in service is an approximation

14.0 Procedures Used To Calculate and Assess Data Quality

This section describes the data quality indicators that are tracked on the Laboratory Information System (LIMS). Equations for precision, accuracy, completeness and method detection limits are provided. Method specific calculations can be found in Laboratory SOPs.

14.1 Precision

Precision is a measure of how well replicate measurements reproduce and can be calculated from laboratory duplicates, instrument duplicates, duplicate analysis of a Laboratory Control Sample (LCS) , method blank duplicates (MBD) or matrix spike duplicates (MSD). Relative percent difference (RPD) is the current measure of precision for most analytes and is calculated as follows:

$$RPD = \frac{(C_1 - C_2)}{m} \times 100\%$$

where: RPD = relative percent difference
C_1 = larger of the two observed values
C_2 = smaller of the two observed values
m = mean of two observed values

If calculated from three or more replicates, relative standard deviation (RSD) is calculated rather than RPD:

RSD = (s/m) X 100%

where: RSD = relative standard deviation
s = standard deviation
m = mean of replicate analyses

Standard deviation is defined as follows:

$$s = \sqrt{\sum_{i=1}^{n} (yi - m)^2 / n-1}$$

where: s = standard deviation
yi = measured value of the ith replicate
m = mean of replicate measurements
n = number of replicates

14.2 Accuracy

Accuracy is a measure of how near a result is to the true value and is expressed as a percent bias or percent recovery. Method accuracy is determined from the analysis of a laboratory control sample, continuing calibration check, quality control check samples or matrix spikes. Method accuracy and matrix effects are assessed by evaluating matrix spike results. The amount of analyte recovered after a sample has been spiked and processed reflects matrix effects upon the accuracy of the method. Percent recovery is calculated from matrix spike results using the following equation:

$$\%R = 100 \times \frac{S - U}{C_{sa}}$$

where: %R = percent recovery
S = measured concentration in spiked aliquot
U = measured concentration in unspiked aliquot
C_{sa} = actual concentration of spike added

The above calculation does not take spike volume into consideration. Lab protocol requires that a <5% volume change occurs when a spike is added negating the need to volume correct.

Percent bias is another measure of accuracy and is calculated using the following equation:

$$\%B = 100 \times \frac{(O-T)}{T}$$

where: %B = percent bias
O = measured concentration of reference material
T = actual concentration of reference material

14.3 Completeness

Completeness is defined as the number of measurements judged valid compared to the number of measurements needed to achieve a specified level of confidence in decision making. The number of measurements judged valid must be determined by laboratory users familiar with the project site, laboratory detection limits, anticipated sample concentrations, and other project, data reduction steps. Measurements judged invalid or suspicious by laboratory staff will be flagged on final laboratory report forms and should be considered in completeness calculation. Laboratory data flags of importance to laboratory users are < "less than" flags and those summarized in Section 5.0 of this manual. Prior to initiating an environmental study lab users should carefully evaluate their project needs in terms of detection limits, accuracy and precision. Specific requests must be addressed in the contract for service (see Section 3.2). The total number of measurements necessary to achieve a specified level of confidence in decision making is determined by laboratory users. Laboratory users need to notify the laboratory if

predetermined criteria are not being met. Completeness is calculated as follows:

$$\% C = 100 \times \frac{V}{n}$$

where: %C = percent completeness
V = number of measurements judged valid
n = total number of measurements necessary to achieve a specified level of confidence in decision making

14.4 Detection Limits

14.4.1 Method Detection Limits

Method Detection Limits (MDLs) are defined in the Federal Register as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte". The Method Detection Limit is a statistical determination of precision only and is not used by the DEC Lab as a reporting limit.

Method Detection Limit studies are part of a new method or technology's initial demonstration of performance if there is a spiking solution available. If a Method requires that MDL studies be performed the study must be repeated at the method required frequency for each sample matrix. This would likely mean that studies would need to be repeated on an annual basis, each time there is a change in the method that affects how the test is performed, or if there is a change in instrumentation. If a frequency of greater than 1/year is suggested, the Laboratory will only perform the study 1/year.

MDLs must meet method-required limits if specified or must be below the laboratory Practical Quantitation Limit (PQL). If a calculated MDL for a parameter exceeds the PQL then the PQL must be raised until results from a new study justify lowering the PQL. If an MDL study is not performed the laboratory may not report to a level lower than the low standard.

Method Detection Limits are determined according to the Federal Register Appendix B Part 136, Revision 1.11. A minimum of seven replicates of low level spiked reagent blanks or solid samples are processed and analyzed as described in the reference listed. The standard deviation of the responses is used to calculate the MDL as follows:

MDL = S(t•99) for n replicates

Where: n = number of replicates analyzed
S = standard deviation of the values
t•99 = student's t value for a one-tailed test at the 99% confidence level for "n" replicates.

A replicate result may not be excluded from the MDL calculation unless it is statistically determined to be an outlier (Dixon's Test for Outliers; α .05, two sided test) or if there is a documented error in the preparation or analysis of the sample. Only the results for the parameters tested to be outliers can be dropped in multi parameter tests. A calculated recovery of 70-130% should be achievable if the MDL is to be used to calculate the PQL. If this level of accuracy is not achieved the concentration of the spike for the study is likely not appropriate and the study should be repeated at a different concentration as soon as possible. This level of accuracy may be difficult to achieve for all parameters in multi-parameter methods.

All method detection limit study results must be imported into the LIMS and the MDL database upon completion. The following information must be included:

- Date of sample analysis and preparation
- Analyst(s) – sample preparation and analysis
- Parameter/matrix
- Method
- Instrument ID
- Spiking level and level of low standard
- Individual results for all of the replicates (including outliers)
- Recalculated results if outliers were excluded (justification must be failure of Dixon Test for outliers)
- Calculated mean, standard deviation and MDL (precision)
- Accuracy (mean of replicate results)

14.4.2 Practical Quantitation Limit

The Practical Quantitation Limit (PQL) is the laboratory reporting level and is synonymous to the TNI term "Limit of Quantitiation (LOQ)". It is a concentration at which both the accuracy and the precision of a method have been taken into consideration. The PQL is generally 2-10 times the calculated MDL. The PQL may be established from variables other then the calculated MDL since the MDL is only an estimation of method precision.

One variable that may be taken into consideration is the concentration of the analyte found in the laboratory reagent or method blank. If background interference cannot be removed the PQL may need to be increased to reflect method inaccuracy at low levels. The laboratory reagent or method

blank processed with the analytical batch should be no greater than 1/2 the concentration of the PQL, with few exceptions..

Another variable that may affect the Reporting Limit is sample dilution as a result of a matrix interference. If a sample dilution is required to remove an interference, the Laboratory PQL increases by the sample dilution factor.

There are alternative approaches to establishing and validating the PQL that may be more practical and appropriate for a given method. If an alternative approach is utilized the protocol must be approved by the DEC Lab Supervisor and Quality Assurance Officer and the protocol and acceptance criteria clearly described in the Method SOP.

The concentration of the low level standard used to calibrate an instrument must be at or below the PQL.

14.4.3 Instrument Detection Limits

Instrument Detection Limits (IDLs) are an estimate of instrument precision. IDL studies are required only when they are method specified. A method requirement for performing an IDL study does not eliminate the TNI requirement of annually verifying the Limit of Quantitation (LOQ). A reagent blank solution is analyzed on three non-consecutive days with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample. IDLs are estimated by calculating the average of the standard deviations of three runs. The IDL only defines the instrumental limitations of a method and does not take the precision of processing and analyzing real samples into consideration.

14.4.4 Limit of Quantitiation

The Limit of Quantitation (LOQ) is a TNI term synonymous to the Laboratory's Practical Quantitation Limit (PQL). The term LOQ will eventually replace the term PQL. Lab policy is to run a standard at or near the PQL (LOQ) with each analytical run. This policy does not apply to tests, for which control samples are not available or appropriate, e.g. pH, temperature.

For tests without sample preparation steps the low level Continuing Calibration Verification (CCV Low) meets NELAC's limit of quantitation verification requirement. The use of the CCVLow to meet the LOQ requirement applies to the following tests: earth metals, alkalinity, chloride, ion chromatography tests, conductivity, silica, total suspended solids, turbidity, ammonia, method 8260, 8021, and TO15. For those tests where the standard curve is prepared from digested standards the CCVLow is equivalent to the LSCLow (see next paragraph) and can be used to meet the laboratory LOQ policy.

The term "Low Level Laboratory Control Sample" (LCS Low) will be used for tests that have sample processing steps. The CCV Low cannot be used as the LSCLow. The LSCLow will need

to be prepared at a concentration at or near the PQL and processed like the samples; a concentration of 1 to 2 times the PQL is the goal for LCS Low. An LCS Low can be prepared from either a primary or second source standard.

14.5 Tracking of Quality Control Data

The LIMS tracks five QC types: spikes, duplicates, standards, blanks and surrogate data. Each QC Type may have sub-categories. The following terms are defined in Section 11.2 of this Plan.

Spike:	Matrix spikes (MS) Laboratory Control Samples (LCS) Low Level Laboratory Control Sample (LCS Low)
Duplicates:	Sample Duplicates (Duplicate) Laboratory Control Sample Duplicates (LCSD) Method Blank Duplicates (MBD) Matrix Spike Duplicates (MSD)
Standard:	Initial Calibration Verification Low Level (ICV Low) Initial Calibration Verification Mid Level (ICV Mid) Initial Calibration Verification High Level (ICV High) Continuing Calibration Verification Low Level (CCV Low) Continuing Calibration Verification Mid Level (CCV Mid) Continuing Calibration Verification High Level (CCV High) Quality Control Standard (QCS)
Surrogates:	
Blanks:	Method Blank (MB) Continuing Calibration Blank (CCB) Initial Calibration Blank (ICB)

14.6 Quality Control Acceptance Criteria

Quality control acceptance criteria were established by reviewing historical data for each method/matrix. The limits meet method specified criteria but are generally narrower. The established limits are annually reviewed and adjusted if necessary.

The validity of established limits can be verified by reviewing data archived on the LIMS. The mean ± 3 standard deviation is used. A minimum of 20 data points should be used to establish limits. When acceptance limits are validated the data set may be tested for outliers. Outliers are not removed prior to

calculating acceptance criteria unless there is a justification. If a data set is from a matrix specific measure of precision or accuracy e.g. matrix spike recovery data, and the data set predominately represents an unusually "clean" or "dirty" matrix from a specific project the Laboratory will look at historical performance and either widen or narrow a calculated acceptance limit to avoid creating an unrealistic window of acceptability. If a method specifies a required acceptance limit the limit must be met unless data is qualified. Laboratory acceptance criteria currently being used are summarized by parameter and matrix in Section 5.0 Quality Assurance Objectives: Tables 5.1 – 5.7. Limits for multi-parameter tests are typically set the same for all parameters. The limit used is most reflective of the majority of parameters.

14.7 Reporting of Quality Control Data

Laboratory analysts assign the appropriate quality control types at the required frequency to a QC Batch. Results are reported into the LIMS by QC Batch at data entry. Relative Percent Difference and Percent Recovery are automatically calculated from the information entered. Paper Laboratory Reports have a "QC Information" summary at the end of each report. Only sample specific QC data is reported on final reports. The Lab Report consolidates all test results for an Order ID that is established at sample log-in. The QC information section of the report summarizes all QC data for Matrix Spikes-MS (percent recovery), Analytical Duplicates – Dup (RPD) and matrix spike duplicates –MSD (RPD) for the entire Order by parameter and Sample Number. When Control Limits are exceeded a flag is added to the QC data. A sample result qualifier or a comment (sample, order or parameter) may also be added to the LIMS if the failed QC result indicates that a sample result(s) may be compromised.

15.0 Corrective and Preventative Actions and Customer Complaints

15.1 Corrective Actions

Corrective actions may be initiated as a result of a problem identified through a system or, performance audit, data review or data end user's request. The process is generally initiated by the Quality Assurance Officer or Laboratory Supervisor and documented on a Quality Assurance Irregularity Report Form (Figure 15.1) by the analyst or Technical Director responsible for the data. The lead analyst has the ultimate responsibility of evaluating the effectiveness of the corrective actions. If a corrective action is ineffective it is the analysts' responsibility to notify the Laboratory Supervisor. Laboratory management must verify that corrective actions have been effective – by performing a follow-up data review, submitting a proficiency sample or performing other internal audit activities. The steps taken in the corrective action process are:

- identify and define the problem
- assign responsibility for investigating the problem
- determine the cause of the problem
- determine the actions needed to eliminate the problem
- implement corrective action
- establish effectiveness of the corrective action
- management verifies effectiveness of corrective action

Corrective action may also be initiated by an analyst during or after analysis of samples. Laboratory personnel are aware that corrective actions may be necessary if:

- Unacceptable or uncharacteristic instrument conditions or calibration or continuing calibration data is generated.
- QC data are outside the warning or control limits for precision and accuracy.
- Peak shapes and or baselines are unacceptable.
- Blank(s) contain target analytes above acceptable levels.
- A surrogate recovery falls outside the expected range.

Investigation of problems revealed by the routine analysis of laboratory QC samples are the responsibility of the analyst generating the data or the Technical Director of the analytical center reviewing the data. Quality control sample results and instrument conditions are checked against established limits and deviations are immediately addressed. Predetermined limits for data acceptability beyond which corrective action may be required can be found in Sections 5 and 8. Additional method specific limits or conditions are described in the Standard Operating Procedures for each of the analytical methods used in the laboratory.

If an analyst determines that corrective actions have not resolved an irregularity and a data set is compromised it is the analyst's responsibility to notify the Technical Director or Laboratory Supervisor

immediately. The Technical Director or Laboratory Supervisor must assess the data and determine if the data is to be released and how it will be qualified. This process is likely to require contact with the client(s) and written instructions on how to proceed. The client's instructions must be retained on file. Irregularity Reports must be completed within two weeks of receipt. The QA Officer and Laboratory Supervisor's review must be completed within two week of receipts. If an analyst is asked to provide additional information or would like to respond to the reviewers comments the Laboratory Supervisor will set-up a meeting within 7 days to address any concerns. The QA Officer will document any discussions or decisions made at the meeting.

15.2 Non-conforming Work

If at any time it is determined that any aspect of the analytical process has compromised the Laboratory's ability to generate defensible data the analyst must notify the Laboratory Supervisor immediately. The Laboratory Supervisor must notify clients in writing within 7 days (e-mail is acceptable) of the irregularity. This policy applies to situations in which the Laboratory Supervisor has determined that the significance of the irregularity justifies recalling work that has already been released or when the Laboratory has decided that it will not report results that are considered invalid. This policy does not apply to those situations in which a data flag or sample note can be used to qualify the data. Corrective actions described in Section 15.1 must be taken immediately to remedy the situation.

15.3 Preventative Actions

All Laboratory staff are encouraged to identify opportunities for improvement and notify management if resources are needed. A Preventative Action Form (Figure 15.2) is available to all Laboratory staff and is used to document needed improvements and potential sources of non-conformance either technical or pertaining to the quality system in general. The form can be found on Y:\DECLab\Administration\forms. Forms are submitted to the Laboratory Supervisor. Preventative actions and follow-up are documented to assure that the preventative action was implemented and successful. Analysts are not allowed to make significant changes to procedures unless approved by the Laboratory Supervisor.

15.4 Customer Complaints

Customer complaint regarding the quality of data or service provided by the Laboratory shall be placed in writing and addressed to the Laboratory Supervisor (e-mails or letters are acceptable). The Laboratory Supervisor is responsible for evaluating the nature of the complaint. Once individuals or systems are identified as being deficient a corrective action will be put into place. The Laboratory Supervisor is responsible for verifying that a corrective action has been implemented and is effective in resolving the customer's complaint. The Laboratory Supervisor must respond to the written complaint in writing in a timely fashion. Complaints and Laboratory responses are kept on file. If a customer is not satisfied with the Laboratory's response the customer has the option of bringing the complaint to the Department Commissioner's attention.

Figure 15.1 - Quality Assurance Irregularity Report

UVM
105 Carrigan Drive
Hills Building – D.E.C. Laboratory
Burlington, VT 05405

Quality Assurance Irregularity Report

Date:	**Due Date:**	**Date Returned:**
Sample ID Number(s) Involved and Study (if applicable):		
Reason for Initiation:		
Description of QA Irregularity:		
Name of Employee who Performed Work:		
Steps taken to investigate irregularity:		
Explanation of probable cause of irregularity:		
Steps taken to prevent future occurrence:		
Reviewers Comments:		

Signature (after review of completed form)	**Form Completion Date(s):**	**Review of completed Form and Signature Date(s):**
Analyst:		
Reviewer:		
Laboratory Supervisor:		

15.2 Preventive Action Plan

Preventive Action Plan

Dan Needham
UVM
105 Carrigan Drive
Hills Building – D.E.C. Laboratory
Burlington, VT 05405

Date Submitted:_____

Response Date: (2 weeks after submittal date)_____

Name of Employee Requesting a Preventative Action:_____

Needed Improvement and Potential Sources of Non-conformance:

Recommended Preventative Action:

Supervisor's Response:

Laboratory Supervisor:_____ **Date:**_____

Employee's Review Response:_____ **Date:**_____

RETURN FORM TO LABORATORY SUPERVISOR

16.0 Quality System Review

16.1 Quality Assurance Reports to Management

The Quality Assurance Officer will provide the Laboratory Supervisor with the following information:

- Laboratory QA Plan Updates (annual or as needed).
- Performance Audit results will be distributed to the Laboratory Supervisor as they become available. Irregularity reports issued as a result of performance audit ratings or other QA Irregularities/deficiencies will be provided to the Laboratory Supervisor and maintained in a central location.
- QA office goals and objectives for the upcoming year (annual performance evaluation/work plan).
- Internal system audit reports from each analytical center (annual).
- Standard Operating Procedure (SOP) status (Appendix A of this document).
- Completed irregularity reports and correspondence related to corrective actions or investigations.

16.2 Laboratory Supervisor's Review of Quality System

TNI requires an annual review of the laboratory's quality system which must be documented. This review must consider:

- Suitability of policies and procedures.
- Technical director's issues and concerns that have been identified in Internal Audit Reports, Preventative Action Plans or Irregularity Reports.
- The outcome of recent internal audits.
- Review all performance audit reports; review and comment on irregularity report, enforce time limits and corrective action implementation.
- The Laboratory Supervisor reviews all SOPs and audit reports.
- The Laboratory Supervisor reviews generated irregularity reports and may initiate a preventative action plan to correct repeated instances of non-conformance.
- The Laboratory Supervisor will make compliance with Laboratory QA Policy part of each analyst's annual review. Continued non-compliance will become a performance evaluation issue.
- Corrective and preventative actions.
- Assessments by external bodies.
- Results of proficiency tests.
- Client feedback/customer complaints.
- Other relevant factors, such as quality control activities, resources and staff training.

Appendix A

Revision No. 15; 1-2013
Standard Operating Procedures
Table of Contents

Appendix B
2009 TNI Standards
Chapter 5 – Chemical Testing
Technical Requirements Instrument Calibration

1.7 Technical Requirements

1.7.1 Initial Calibration

1.7.1.1 Instrument Calibration

This module specifies the essential elements that shall define the procedures and documentation for initial instrument calibration and continuing instrument calibration verification to ensure that the data shall be of known quality for the intended use. This Standard does not specify detailed procedural steps ("how to") for calibration, but establishes the essential elements for selection of the appropriate technique(s). This approach allows flexibility and permits the employment of a wide variety of analytical procedures and statistical approaches currently applicable for calibration. If more stringent standards or requirements are included in a mandated method or by regulation, the laboratory shall demonstrate that such requirements are met. If it is not apparent which Standard is more stringent, then the requirements of the regulation or mandated method are to be followed.

The following items are essential elements of initial instrument calibration:

a) the details of the initial instrument calibration procedures including calculations, integrations, acceptance criteria and associated statistics shall be included or referenced in the method SOP. When initial instrument calibration procedures are referenced in the method, then the referenced material shall be retained by the laboratory and be available for review;

b) sufficient raw data records shall be retained to permit reconstruction of the initial instrument calibration (e.g., calibration date, method, instrument, analysis date, each analyte name, analyst's initials or signature; concentration and response, calibration curve or response factor; or unique equation or coefficient used to reduce instrument responses to concentration);

c) sample results shall be quantitated from the initial instrument calibration and may not be quantitated from any continuing instrument calibration verification unless otherwise required by regulation, method or program;

d) all initial instrument calibrations shall be verified with a standard obtained from a second manufacturer or from a different lot. Traceability shall be to a national standard, when commercially available;

e) criteria for the acceptance of an initial instrument calibration shall be established (e.g., correlation coefficient or relative percent difference). The criteria used shall be appropriate to the calibration technique employed;

f) the lowest calibration standard shall be at or below the LOQ. Any data reported below the LOQ shall be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or explained in the narrative,

g) the highest calibration standard shall be at or above the highest concentration for which quantitative data are to be reported. Any data reported above the calibration range shall be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or explained in the narrative;

h) the following shall occur for instrument technology (such as ICP or ICP/MS) with validated techniques from manufacturers or methods employing standardization with a zero point and a single point calibration standard:

   i. Prior to the analysis of samples; the zero point and single point calibration standard shall be analyzed and the linear range of the instrument shall be established by analyzing a series of standards, one of which shall be at or below the LOQ. Sample results within the established linear range will not require data qualifiers.

   ii. A zero point and single point calibration standard shall be analyzed with each analytical batch.

   iii. A standard corresponding to the limit of quantitation shall be analyzed with each analytical batch and shall meet established acceptance criteria.

   iv. The linearity is verified at a frequency established by the method and/or the manufacturer.

i) if the initial instrument calibration results are outside established acceptance criteria, corrective actions shall be performed and all associated samples re-analyzed. If re-analysis of the samples is not possible, data associated with an unacceptable initial instrument calibration shall be reported with appropriate data qualifiers; and

j) if a reference or mandated method does not specify the number of calibration standards, the minimum number of points for establishing the initial instrument calibration shall be three.