QUALITY MANUAL

for

State of Florida

Department of Environmental Protection

Laboratory

FDOH Certification Number E31780

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Quality Manual for

State of Florida

Department of Environmental Protection

Laboratory

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Florida DEP Laboratory

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Table of Contents

QA Plan Elements

Contents	Description	Page #
	Title Page	1
	Table of Contents	6
	List of Figures	8
	List of Tables	8
	Acronyms	9
1.0	Introduction, Scope and Applicability	13
	1.1 Introduction	13
	1.2 Scope	13
	1.3 Applicability	13
2.0	References	13
3.0	Terms and Definitions	14
4.0	Management Requirements	14
	4.1 Organization	14
	4.2 Management System	16
	4.3 Document Control	27
	4.4 Review of Requests, Tenders and Contracts	28
	4.5 Subcontracting of Environmental Tests	29
	4.6 Purchasing Services and Supplies	29
	4.7 Services to the Client	30
	4.8 Complaints	31
	4.9 Control Of Non-conforming Environmental Test Work	31
	4.10 Improvement	31
	4.11 Corrective Action	32
	4.12 Preventive Action	33
	4.13 Control of Records	33
	4.14 Internal Audits	38
	4.15 Management Reviews	39
	4.16 Data Integrity Investigations	40

Contents	Description	Page #
5.0	Technical Requirements	40
	5.1 General	40
	5.2 Personnel	40
	5.3 Accommodation and Environmental Conditions	42
	5.4 Environmental Test Methods and Method Validation	42
	5.5 Calibration Requirements	46
	5.6 Measurement Traceability	47
	5.7 Collection of Samples	48
	5.8 Handling Samples and Test Items	49
	5.9 Quality Assurance for Environmental Testing	54
	5.10 Reporting Results	62
Appendix A	Roles and Responsibilities for the Chemical Agent Laboratory	65
	1.1 Laboratory Director	65
	1.2 Laboratory Manager	65
	1.3 Chemical Agent Hygiene Officer	66
	1.4 Agent Manager	67
	1.5 Chemical Agent Operators	67
	1.6 Inventory Witness	68
Appendix B	Chemistry Essential Quality Controls	69
	1.0 Introduction	69
	2.0 Scope	69
	3.0 Terms and Definitions	69
	4.0 Method Selection	69
	5.0 Method Validation	69
	6.0 Demonstration of Capability	71
	7.0 Technical Requirements	73
Appendix C	References	79

LIST OF FIGURES

Figure Number	Description	Page Number
4.1	Chemistry Program Organization Chart	22
4.2	Biology Program Organizational Chart	23
4.3	Laboratory Support Program Organization Chart	24
4.4	DEP Task Assignment Form	29
4.5	Sampling Kit Packing List	35
4.6	Chain of Custody Record	35
4.7	Laboratory Custody Log	35
5.1	Sample Backlog Report	54

LIST OF TABLES

Table Number	Description	Page Number
4.1	Corrective Actions in Biology	32
4.2	Preventive Maintenance – Biology	33
4.3	Laboratory Waste Disposal Procedures	36
5.1	Chemistry QA Targets for MDL/PQL, Precision and Accuracy	42
5.2	Biology QA Targets for MDL/PQL, Precision and Accuracy	42
5.3	Biology Instrument Calibration	46
5.4	Laboratory Reagent Storage	48
5.5	Biology Sampling Equipment	48
5.6	Sample Containers, Preservation Techniques and Hold Times	54

ACRONYMS

ACS	American Chemical Society
ADaPT	Automated Data Processing Tool
AGP	Algal Growth Potential
AM	Agent Manager
AMU	Atomic Mass Unit
BETX	Benzene, Ethyl benzene, Toluene and Xylenes
BFB	Bromofluorobenzene (used for mass spectral tuning)
BNA	Base/Neutral, Acid Extractables
BOD	Biochemical Oxygen Demand
CA	Chemical Agent
CAHO	Chemical Agent Hygiene Officer
CAO	Chemical Agent Operator
CAS Number	Chemical Abstract Services Number
CBOD	Carbonaceous Biochemical Oxygen Demand
CCC	Continuing Calibration Compounds
CCCS	Continuing Calibration Check Standard
CCV	Continuing Calibration Verification
CFR	Code of Federal Regulations
CHO	Chemical Hygiene Officer
CHP	Chemical Hygiene Plan
CI	Chemical Ionization
CLP	Contract Laboratory Program
cm	Centimeter
COD	Chemical Oxygen Demand
COR	Contract Officer's Representative
CV	Coefficient of Variation
CVAAS	Cold Vapor Atomic Absorption Spectrometry
CVAFS	Cold Vapor Atomic Fluorescence Spectrometry
DL	Detection Limit
DF	Dilution Factor
DFTPP	Decafluorotriphenyl Phosphine
DOT	Department of Transportation
DSHP	Dilute Solution Hygiene Plan
ECBC	U.S. Army Edgewood Chemical and Biological Center and Engineering Center
ECD	Electron Capture Detector
EI	Electron Ionization
EICP	Extracted Ion Current Profile (plot of ion abundance vs. time)
EPA	Federal Environmental Protection Agency
ERLN	Environmental Response Laboratory Network
FAC	Florida Administrative Code
DEP	Florida Department of Environmental Protection

DOH	Florida Department of Health
GC	Gas Chromatograph
GC/AFD	Gas Chromatograph/Atomic Fluorescence Detection
GC/MS	Gas Chromatograph/Mass Spectrometry
GLP	Good Laboratory Practice
HPLC	High Pressure Liquid Chromatography
Hz	Hertz
I.D.	Internal Diameter
IC25	Inhibiting Concentration 25 (chronic toxicity)
ICAL	Initial Calibration
ICCS	Initial Calibration Check Standard
ICP	Inductively Coupled Plasma
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ID	Identification
IR	Infrared
IS	Internal Standard
ISE	Ion Selective Electrode
ISO	International Standards Organization
IUPAC	International Union of Pure and Applied Chemistry
L	Liter
LC	Liquid Chromatography
LC50	Lethal Concentration 50 (acute toxicity)
LCS	Laboratory Control Sample
LFB	Laboratory Fortified Blank
LIMS	Laboratory Information Management System
LN	Limiting Nutrient
LM	Laboratory Manager
LOD	Limit of Detection
LOEC	Lowest Observed Effect Concentration (chronic toxicity)
LOQ	Limit of Quantitation
m	Meter
MDL	Method Detection Limit
MS	Mass Spectrometry
MS/MS	Triple Quadrupole Mass Spectrometry
MSD	Matrix Spike Duplicate or Mass Selective Device
MW	Molecular Weight
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute for Standards and Technology
NOEC	No Observed Effect Concentration (chronic toxicity)
NPD	Nitrogen Phosphorus Detector
NPDES	National Pollution Discharge Elimination System

NTU	Nephelometric Turbidity Units
ON	Original Number (of organisms used in toxicity tests)
OTIS	Office of Technology and Information Services
ºC	Degrees Celsius
P&T	Purge and Trap
PDF	Portable Document Format
PE	Performance Evaluation
PFAS	Perfluoroalkyl Substances
$PM_{2.5}$	Particulate Matter ≤ 2.5 Microns
ppb	Parts per billion
PPE	Personnel Protective Equipment
ppm	Parts per million
ppt	Parts per trillion
PQL	Practical Quantitation Limit
PT	Proficiency Testing
PTFE	Polytetrafluoroethylene
QA/QC	Quality Assurance/Quality Control
QAP	Quality Assurance Plan
QATs	Quality Assurance Targets
QCCS	Quality Control Check Standard
QM	Quality Manual
qPCR	Quantitative Polymerase Chain Reaction
RCRA	Resource Conservation and Recovery Act
RF	Radio Frequency; Response Factor
RL	Reporting Limit
RPD	Relative Percent Difference
RRF	Relative Response Factor
RRT	Relative Retention Time
RSD	Relative Standard Deviation
RT	Retention Time
S/N	Signal-to-Noise Ratio
SARA	Superfund Amendments and Reauthorization Act
SD	Standard Deviation
SIM	Selective Ion Monitoring
SOP	Standard Operating Procedure
SPCC	System Performance Check Compounds
SPLP	Synthetic Precipitation Leaching Procedure
SRT	Standard Reference Toxicant
TCLP	Toxicity Characteristic Leaching Procedure
TIC	Total Ion Current; Tentatively Identified Compound
TNI	The NELAC Institute
UDA	Ultra-Dilute Agent
UHP	Ultra-High Purity

VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
WET	Whole Effluent Toxicity
WIN	Water Information Network
ZHE	Zero Headspace Extraction

1.0 INTRODUCTION, SCOPE AND APPLICABILITY

1.1 INTRODUCTION

The Florida Department of Environmental Protection (DEP) Laboratory's mission is to aid in the protection of Florida's environment by providing legally defensible and scientifically credible analytical and technical support to the department. Information generated by the Laboratory is fundamental to the department in carrying out its mission to preserve, protect, conserve, and restore the air, water, and natural resources of the state. The Laboratory's management is committed to generating data of the highest quality necessary for fulfilling the mission of the Laboratory.

1.2 SCOPE

The DEP Laboratory is a full service environmental laboratory which provides chemical and biological analytical support to the following:

a. departmental programs
b. district operations
c. water management districts
d. environmental operations of other local (city, county) and state agencies and commissions
e. local, state, and federal law enforcement agencies

The Laboratory also provides chemical and biological analytical consulting services to the above listed programs. The quality system and technical requirements of tests and methods performed in the laboratory conform to the requirements of the 2016 TNI Standard, Volume 1, Rev. 2.1, except where stated otherwise.

1.3 APPLICABILITY

This document serves as the Quality Manual (QM) for the Chemistry, Biology and Scientific Support Programs of the Laboratory. The quality system and technical requirements described in this document are applicable to all fields of accreditation (FOA) for which the Laboratory is certified. The Florida Department of Health, Environmental Laboratory Certification Program is the Laboratory's primary accreditation body.

2.0 REFERENCES

See Appendix C.

3.0 TERMS AND DEFINITIONS

The relevant definitions from the 2016 TNI Standard, Volume 1, Rev. 2.1, Module 2, Section 3.0 are the preferred references. See the 2016 TNI Standard. Definitions related to this document that are used differently or do not exist in the above references are defined in the text.

4.0 MANAGEMENT REQUIREMENTS

4.1 ORGANIZATION

4.1.1 The Laboratory is part of the Division of Environmental Assessment and Restoration of the Florida Department of Environmental Protection. The Laboratory is located at the Bob Martinez Center, Jerry Edward Brooks Building, 2600 Blair Stone Road, Tallahassee, FL 32399-2400. The telephone number is (850) 245-8085. The Florida Department of Health (FDOH) Certification Number is E31780.

4.1.2 This Quality Manual (QM) in conjunction with the Standard Operating Procedures (SOPs) provides guidance for laboratory operations and serves as the document that defines the criteria necessary to meet the standards of TNI. This QM details the activities and evaluation criteria necessary to ensure that analytical data reported by the laboratory meet the requirements of the 2016 TNI Standard, Volume 1, Rev. 2.1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis*. This QM also documents procedures intended to ensure that all data are of high and known quality in order to meet the scientific objectives of the department.

4.1.3 Unless otherwise agreed upon with the customer in order to meet the objectives of a given project, the management system described in this document is applicable to all chemistry and biology tests performed by the facility described in 4.1.1.

4.1.4 The responsibilities of key personnel are outlined in section 4.1.5 of the QM. These responsibilities are performed by the key personnel identified or duly delegated representatives.

4.1.5 The DEP Laboratory:

(a) Has management and technical personnel with the educational background, authority and technical resources at their disposal to carry out their duties, including the implementation, maintenance, and improvement of the management system. The Laboratory's QA officer conducts an annual management review per Standard Operating Procedure SOP LB-010, *Quality System Management Review*, to ensure the maintenance of data integrity, quality, and efficiency.

(b) Requires that all Laboratory employees are responsible and conduct themselves in a manner that does not impact the competence and operational integrity of the Laboratory as outlined in SOP LB-012, *Code of Ethics*.

(c) Is subject to Chapter 119 of Florida Statutes; therefore, all records and documents generated by the DEP Laboratory, unless otherwise exempted by Chapter 119, Florida Statutes, are public records and may be subject to disclosure per the guidelines and exceptions published in said Chapter. The Laboratory cannot guarantee the confidentiality of reports transmitted electronically or by facsimile.

(d) Has a data integrity training program (See section 5.2.7).

(e) Has a defined organizational structure including quality management, support services, and technical operations, see Figure 4.1 (Chemistry Organization Chart), Figure 4.2 (Biology Organization Chart) and Figure 4.3 (Laboratory Support Organization Chart).

(f) Maintains job descriptions for all employees. See Figures 4.1, 4.2, and 4.3 for the responsibilities of key personnel.

(g) Annually reviews and updates (if necessary) all SOPs. The protocol for updating and reviewing SOPs is described in SOP LB-001, *Protocol for Preparing Standard Operating Procedures*, and in SOP LB-010, *Quality System Management Review*. Any updates to SOPs must have the approval of the supervisor responsible for the procedure contained in said SOP and must conform to the policies of the Laboratory. It is the responsibility of Laboratory supervisors to ensure proper documentation demonstrating that their employees have read, understood, and are using the latest versions of SOPs and that this is documented in the LIMS training module. The latest official versions of SOPs are only located on the DEP Internet site and are accessible to all analysts and technicians throughout the Laboratory. Laboratory analysts are required to successfully analyze initial and on-going demonstrations of capability according to Appendix B, section 6.0.

(h) Has technical management as identified in section 4.1.7.2.

(i) Has a full time designated Quality Assurance Officer. See section 4.1.7.1 for a description of responsibilities.

(j) Has alternate supervisors who, in the absence of key management personnel, are assigned to assume their responsibilities. In the absence of the Deputy Division Director, the Program Administrators will assume his duties.

(k) Has ethics training described in section 5.2.7 emphasizing the importance of the activities of each employee and the ramifications of them not performing their responsibilities according to laboratory procedures and policies.

4.1.6 A Quality System Management Review takes place annually to ensure that management holds regular staff meetings to discuss quality issues, workload and staffing issues, and other items of importance to the Laboratory. Necessary changes to the quality system as a consequence of performance on proficiency samples, round robins, split samples, or audits are discussed for incorporation and implementation. See SOP LB-010, *Quality System Management Review*, for further information.

4.1.7 Additional requirements

4.1.7.1 The Quality Assurance Officer or his designee:

(a) serves as the primary contact for oversight and review of quality control data;

(b) conducts all QA responsibilities independent of other laboratory operations;

(c) conducts oversight of QA data without outside influence;

(d) has experience in QA/QC procedures and the Laboratory Quality System;

(e) has experience with the analytical methods;

(f) conducts annual internal audits;

(g) monitors QA/QC activities of the Laboratory and notifies management of deficiencies;

(h) monitors and ensures corrective actions are effective.

4.1.7.2 The technical managers in the Chemistry and Biology Programs exercise day-to-day supervision over their staff and are responsible for the operations of their respective groups and laboratories. The Deputy Division Director and Program Administrators are responsible for the DEP Laboratory. If a technical manager is absent for more than fifteen (15) consecutive calendar days, the manager will designate another manager or full-time senior staff member meeting the necessary qualifications to assume his/her responsibilities. If the absence exceeds thirty-five (35) days, the accreditation body will be notified in writing.

4.2 MANAGEMENT SYSTEM

4.2.1 Description

The Laboratory is part of the Division of Environmental Assessment and Restoration. The Laboratory is comprised of Chemistry and Biology Programs and a Laboratory Support Program. Each Program is managed by a Program Administrator who reports directly to the Deputy Division Director.

CHEMISTRY

The Chemistry Program is divided into two subsections: organic analysis and inorganic analysis. The Program is headed by a Program Administrator, who is responsible for both the technical and administrative direction of the program. The Program Administrator and the Quality Assurance Officer are committed to the QA program described in this plan. See Figure 4.1 for the organizational structure.

The analytical subsections are headed by Environmental Administrators who are responsible for ensuring their staff are cognizant of the objectives and requirements of the QM and SOPs and that data submitted to the QA Officer or Program Administrator meet these requirements. Each Environmental Administrator is supported by Environmental Managers

responsible for all bench analysts and technicians in their group. The inorganics subsection is divided into three work groups; nutrients, general chemistry, and metals. The organics subsection consists of the volatiles, semi-volatile, and pesticide work-groups.

BIOLOGY

The Biology Program is divided into four subsections: bench biology, toxicity, molecular biology and taxonomy. The Program is headed by a Program Administrator, who is responsible for both the technical and administrative direction of the program. The Program Administrator and the Quality Assurance Officer are committed to the QA program described in this plan. See Figure 4.2 for the organizational structure.

Analytical subsections are headed by Environmental Administrators responsible for ensuring their staff are cognizant of the objectives and requirements of the QM and SOPs and that data submitted to the QA Officer or Program Administrator meet these requirements. Each Environmental Administrator is supported by Environmental Managers responsible for all bench analysts and technicians in their subsection. The bench biology subsection performs chlorophyll, microbiological, and biochemical oxygen demand (BOD) analyses. The toxicity subsection performs whole effluent toxicity (WET) bioassays, algal growth potential (AGP) bioassays, and limiting nutrient (LN) bioassays. The molecular subsection performs quantitative polymerase chain reaction (qPCR) analysis. The taxonomy subsection performs algal and aquatic macroinvertebrate taxonomic identifications.

Organization and Management of Ultra-Dilute Chemical Agent Facility

The Florida Department of Environmental Protection has been selected to participate in a national network of laboratories known as the Environmental Response Laboratory Network (ERLN). This network is one of several laboratory networks established through Presidential directives to ensure that critical services are available to support response and recovery operations following an emergency of national significance or terrorist attack. The ERLN is administered by the U.S. Environmental Protection Agency with support from the U.S. Department of Homeland Security.

The roles and responsibilities of the management and staff involved with work performed for the ERLN are provided in Appendix A.

Scientific Support Services Program

The Scientific Support Services Program (SSSP) has four primary functions; data support, laboratory quality assurance, sample support, and health/safety/infrastructure support. The -sample support function is supervised by an Environmental Administrator that reports directly to the Program Administrator. See Figure 4.3 for the organizational structure.

4.2.2 Quality Policy Statement

The DEP Laboratory's mission is to aid in the protection of Florida's environment by providing legally defensible and scientifically credible analytical and technical support to the department and other customers. All Laboratory personnel concerned with the testing and

measurement of environmental samples familiarize themselves with the Laboratory's quality documentation and are trained to implement these policies and procedures as described in the Laboratory's QA Manual and Standard Operating Procedures (SOPs). The Laboratory's management is committed to compliance with NELAC standards and good professional practice and to implement policies and procedures that generate data of the highest quality necessary for fulfilling the mission of the Laboratory.

4.2.3 Management Commitment

The Laboratory's management is committed to generating data of the highest quality necessary for fulfilling the mission of the Laboratory and satisfying customer expectations.

Laboratory

David D. Whiting, M.S., Deputy Division Director
Directs all administrative and technical activities of the Laboratory.

Chemistry Program

Colin Wright, Ph.D., Chemistry Program Administrator
The Program Administrator directs activities of the Chemistry Program and serves as Chief Chemist for the department. Reviews, certifies and signs analytical reports for release to clients. Serves as the Laboratory Director for the ERLN Ultra-Dilute Chemical Agent Laboratory.

Liang-Tsair Lin, Ph.D., Environmental Administrator
Supervises the organic chemistry subsection. Responsible for results generated from analyses of water, soil/sediment, tissue, and waste samples submitted for pesticide, volatile, and semi-volatile organic analyses. Ensures compliance with quality control and laboratory quality assurance objectives. Reviews, certifies and signs analytical reports for release to clients. Serves as the Assistant Laboratory Director for the ERLN Ultra-Dilute Chemical Agent laboratory.

Dr. rer. nat. Bettina Steinbock, Environmental Administrator
Supervises the nutrients and general chemistry subsections. Responsible for results generated from analyses of water, soil, tissue, and waste samples submitted for inorganic analyses including nutrient, general chemistry, and major anion content and other related analyses. Ensures compliance with quality control objectives and laboratory quality assurance in the inorganic subsection. Reviews, certifies and signs analytical reports for release to clients.

Chris Bowen, B.S., Environmental Administrator
Supervises the metals analysis subsection. Responsible for results generated from metals analyses of water, soil, tissue, and waste samples submitted to the laboratory. Ensures compliance with quality control objectives and laboratory quality assurances in the metals group.

Irina Carbone, Ph.D., Environmental Manager
Supervises a subset of analysts within the nutrients and general chemistry group. Responsible for results generated from analyses of water, soil, tissue, and waste samples submitted for inorganic tests including nutrients, general chemistry, and major anion content and other related analyses. Ensures compliance with quality control objectives and laboratory quality assurance in the nutrients and general chemistry group.

Kerry Tate, Ph.D., Environmental Administrator
Supervises the volatile organic and semi-volatile organic subsections. Responsible for analytical work generated from the analysis of environmental samples submitted to the laboratory for measurement of organic pollutants. Ensures compliance with laboratory quality control objectives, laboratory quality assurance and waste management procedures in the organic chemistry groups. Reviews, certifies, and signs analytical reports for release to clients. Serves as the Laboratory Manager, Agent Manager, and Co-Chemical Agent Hygiene Officer for the ERLN Ultra-Dilute Chemical Agent Laboratory.

Figure 4.1 shows an organizational chart of the management staff of the Chemistry Program.

Biology Program

Cheryl Swanson, M.S., Biology Program Administrator
The Program Administrator directs the activities of the Biology Program. Serves as a department's lead in issues relating to harmful algal blooms (HABs) and aquatic toxicity. Responsible for overseeing all issues related to personnel, budget, infrastructure, workload, and analytical services within the Biology Program. Coordinates document review and technical services for other agency programs. Represents the Biology Program in meetings with clients and management. Reviews, certifies and signs analytical reports for release to clients.

Jackie Savage, B.S., Environmental Administrator
Supervises the bench biology and toxicity subsections. Responsible for results generated from analyses of water and soil samples submitted for chlorophyll, microbiological, biochemical oxygen demand (BOD), WET bioassays, AGP bioassays, and LN bioassays. Ensures compliance with quality control objectives and laboratory quality assurance. Provides technical assistance and document review for DEP staff and external stakeholders. Reviews, certifies, and signs analytical reports for release to clients.

Puja Jasrotia, Ph.D., Environmental Administrator
Supervises the molecular and taxonomy subsections. Responsible for results generated from analyses of environmental samples submitted for qPCR, algal identification, and aquatic macroinvertebrate identification. Ensures compliance with quality control objectives and laboratory quality assurance. Provides technical assistance and document review for DEP

staff and external stakeholders. Reviews, certifies, and signs analytical reports for release to clients.

Diane Power, B.A., Environmental Manager
Supervises the bench biology subsection. Responsible for results generated from analyses of water and soil samples submitted for chlorophyll, microbiological, and biochemical oxygen demand (BOD). Ensures compliance with quality control and laboratory quality assurance objectives. Reviews documents submitted to the department for technical merit.

Lauren Gottfreid, B.S., Environmental Manager
Supervises the toxicity subsection. Responsible for results generated from analyses of effluent samples submitted for WET bioassay analysis, AGP bioassay analysis, and LN bioassay analysis. Ensures compliance with quality control and laboratory quality assurance objectives. Reviews documents submitted to the department for technical merit.

Sarah Menz, Ph.D., Environmental Manager
Supervises the molecular subsection. Ensures compliance with quality control and laboratory quality assurance objectives. Responsible for results generated from analyses of environmental samples submitted for qPCR analyses. Reviews documents submitted to the department for technical merit.

Amelia Rankin, B.S., Environmental Manager
Supervises the taxonomy subsection. Responsible for results generated from analyses of environmental samples submitted for algal and aquatic macroinvertebrate identification. Ensures compliance with quality control and laboratory quality assurance objectives. Serves as a contact for harmful algal blooms (HABs) sampling and analytical services. Coordinates field sampling services for the laboratory. Reviews documents submitted to the department for technical merit.

Figure 4.2 shows an organizational chart of the management staff of the Biology Program.

Scientific Support Services Program

Kathleen Lurding, M.S., Program Administrator
Directs the Laboratory's Support Program. Supervises professional, technical, and clerical staff as required. Oversees the design, construction, testing, and implementation of data acquisition and management applications. Oversees user training. Consults with laboratory staff on hardware and software purchases. Provides technical assistance to DEP staff and external stakeholders on issues of data management and assessment.

John Watts, B.S., Environmental Administrator
Serves as a Project Manager for the Laboratory. Is the customer contact point in scheduling sample analyses and in responding to customer inquiries. Supervises operation of the laboratory receiving workgroup.

Plans, coordinates, and directs staff and/or contractors in the development or acquisition of computer software for use by the Laboratory. Acts as the Web Administrator for the laboratory, overseeing the maintenance of information available to the Department and the public sector and the development of web-based tools for retrieving or storing information.

Magan Bowden, Environmental Specialist III
Serves as a Project Manager for the laboratory. Is the contact for the South Florida Water Management District (SFWMD) for scheduling sample analyses and for responding to customer inquiries. Manages overflow workload and serves as a liaison between the laboratory support section and DEP Field Operations staff. Assists in the management of the laboratory receiving workgroup.

T. M. Chandrasekhar, Ph.D., Quality Assurance Officer/Environmental Consultant
Serves as the laboratory's Quality Assurance Officer. Initiates and oversees all internal QA/QC audits. Manages the laboratory's blind proficiency testing program and maintenance of the Laboratory's SOPs. Evaluates quality control results, corrective actions, and establishes policy for laboratory quality management. Reviews, certifies, and signs analytical reports.

Nhon Vo, Engineering Specialist IV
Plans, designs, and coordinates building renovations and construction for the DEP Laboratory. Coordinates and maintains the building mechanical and electrical systems overseeing upgrades and repair. Serves as the Property Inventory Officer, the Division Health and Safety Officer, the Hazardous Waste Coordinator, the Radiation Safety Officer, and the Co-Chemical Agent Hygiene Officer for the ERLN Ultra-Dilute Chemical Agent Laboratory.

Figure 4.3 shows an organizational chart of the management staff of the Laboratory Scientific Support Services Program.

Figure 4.1

Chemistry Program Organizational Chart

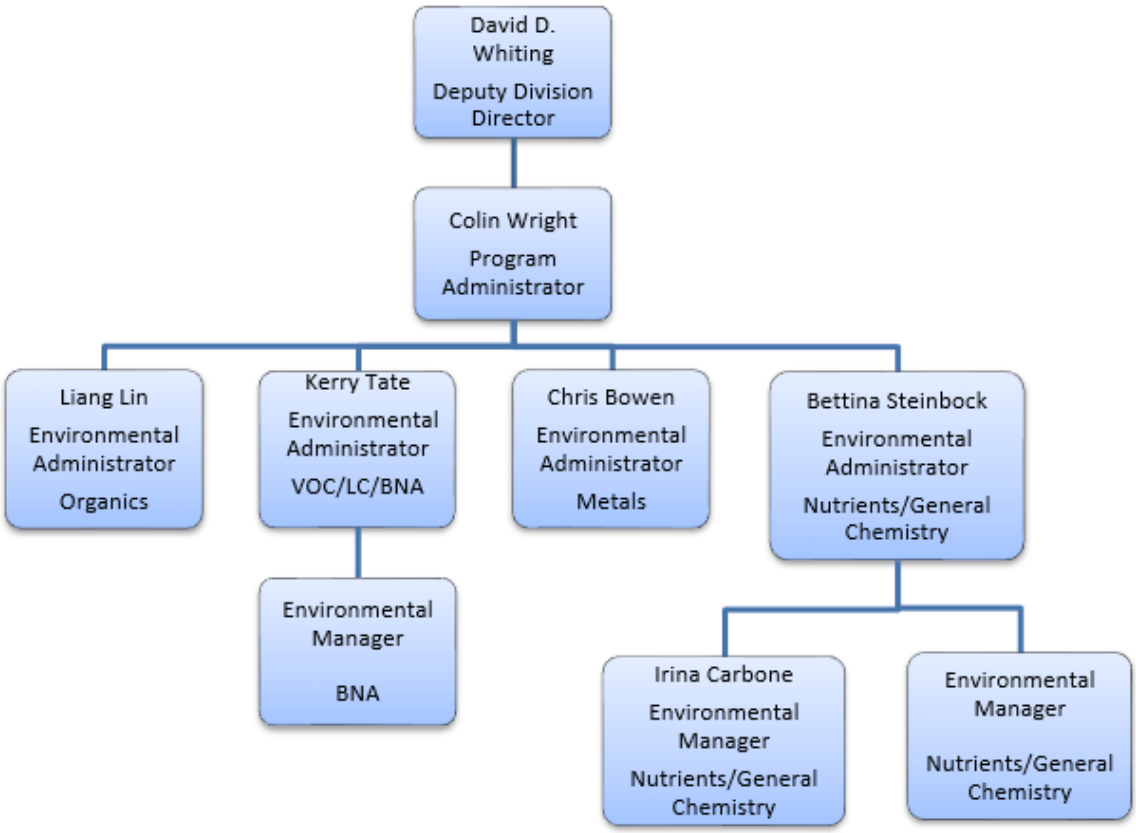


Figure 4.2

Biology Program Organizational Chart

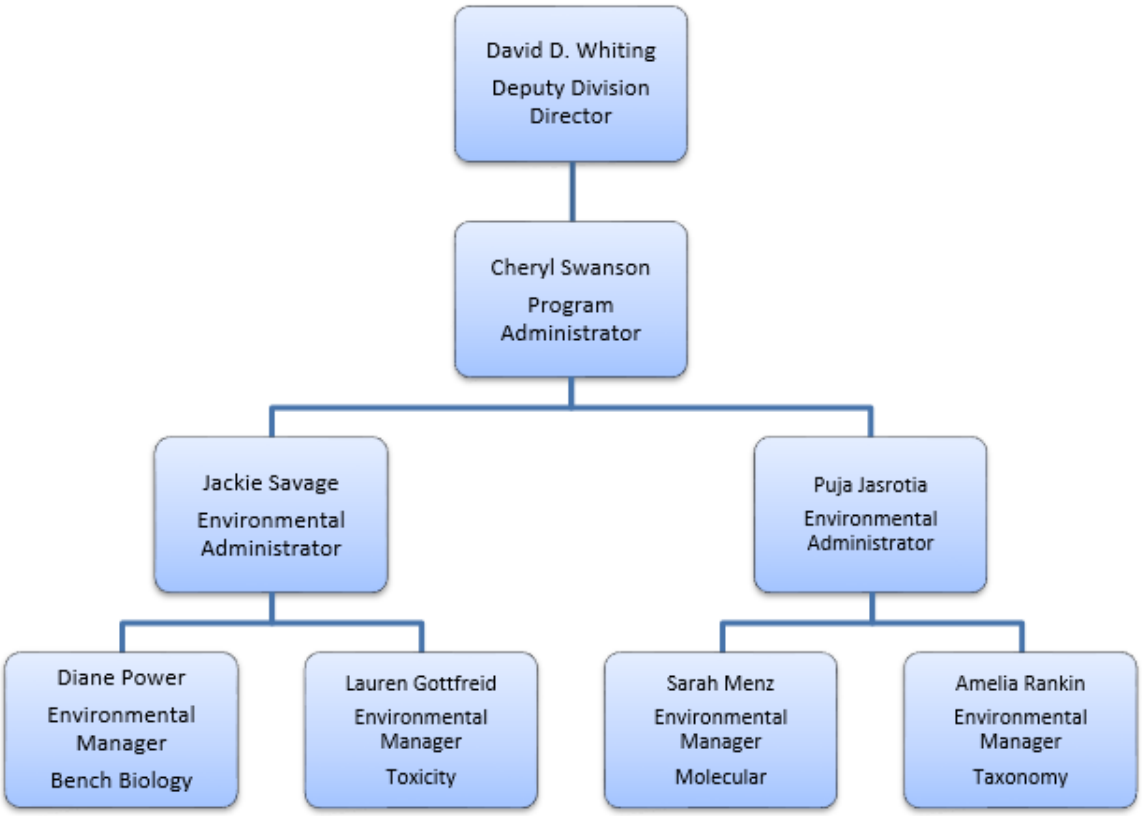
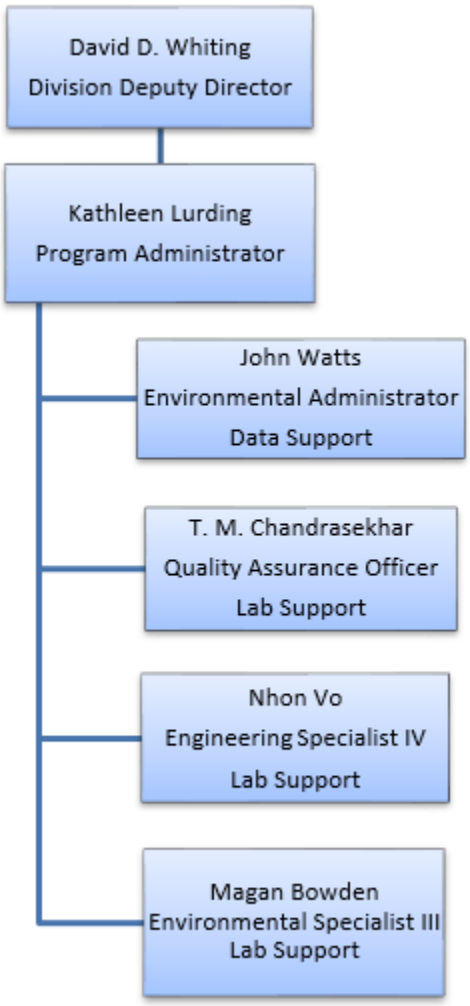


Figure 4.3

Scientific Support Services Program Organizational Chart



4.2.4 Meeting Customer Requirements

Samples must be scheduled with the Laboratory prior to acceptance. The decision to formally accept samples is based on the client's expectations for analytical methods, turnaround times, laboratory capacity, sensitivity, and confidentiality (for criminal events). All scheduled work is reviewed by Chemistry and Biology Program environmental administrators or the Project Manager prior to approval for receipt by the Laboratory. Samples are accepted for analysis by logging them into the LIMS and assigning tests.

See SOP LB-018, *Standard Operating Procedure for Using the LIMS Scheduler*. The LIMS software system for scheduling samples allows customers to schedule sampling events up to eleven months ahead of the event.

See SOP LB-028, *Standard Operating Procedure for Tracking Priority Projects,* for details on how priority projects are handled and clients are kept informed of progress.

The customer is notified of any non-conformances that may affect the integrity of the data. The samples are analyzed unless the customer requests otherwise or the nature of the non-conformance makes analysis impractical. Data from compromised samples are flagged with the appropriate qualifier(s) or comments and/or a non-conformance report is issued with the analysis report, depending on the nature of the issue. The Laboratory non-conformance system procedures are described in SOP LB-002, *Non-Conformance Reporting System*.

Significant deviations from standard policies or practices of the Laboratory are reported to the client and documented with the analytical reports. Any samples that are prepared or analyzed beyond accepted holding times have a statement automatically stamped with the data alerting the client to the fact that tests were conducted after the sample had expired. Similarly, failure of any quality control checks is commented with the data, directing the client to the Quality Control Report for details of failures. Data qualifiers are used to alert clients of quality control problems and holding time exceedances.

Accepted samples that were improperly preserved are documented in the LIMS and analytical reports as sample-level comments and/or in a LIMS non-conformance report. Results reported from improperly preserved samples are also appropriately qualified according to SOP LB-027, *Reporting Qualified Data and Correcting Quality Control Problems*. All other significant observations that do not conform to accepted practices or policies are documented and reported along with analytical results. Those documents may be as letters, interoffice memoranda, or appendices to analytical reports. Sample integrity non-conformances such as improper temperature and pH preservation, insufficient volume, leaking or broken bottles, etc., are entered into a non-conformance report in the LIMS as well as documented on a log-in checklist with the log-in technician's initials.

4.2.5 Technical and Supporting Procedures

Laboratory SOPs are divided into three groups, Chemistry, Biology, and the Laboratory as a whole. Current revisions of all SOPs (PDF files) can be accessed at

https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops.

Printed copies are not considered by the Laboratory to be official SOPs. For the purpose of reviewing and revising SOPs annually, copies of current revisions (Word) can be saved to the reviewer's computer from \\FLDEP1\DEAR\Labs\SOPs. The versions stored on FLDEP1 are locked and maintained for archival purposes only. The format of the SOPs is detailed in SOP LB-001, *Protocol for Preparing Standard Operating Procedures (SOPs).*

4.2.6 The responsibilities of all supervisors within the Laboratory can be found in the appropriate job descriptions detailed in section 4.2.3. Personnel authorized to certify reports are stipulated in these job descriptions.

4.2.7 All Laboratory personnel are required to annually review and update (if necessary) all SOPs that pertain to the work they perform within the laboratory (SOP LB-010). See section 4.1.5 (g) for further information on notifying personnel of system changes.

4.2.8 Additional Management System Requirements

4.2.8.1 See section 5.2.7 for a description of the Laboratory Data Integrity System.

4.2.8.2 The Quality Assurance Officer is responsible for keeping the Laboratory QM up to date. The QM is reviewed and revised at least annually and posted to the Laboratory's web site at: https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops.

Revisions are approved through the laboratory supervisors and forwarded to the Quality Assurance Officer for incorporation into the QM. The posted version is the latest official version of the QM.

4.2.8.3 This QM along with the Laboratory SOPs detail the Laboratory's Quality System. This document contains all the mandatory information required by section 4.2.8.3 of the TNI standards Volume 1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis*, Module 2: Quality Systems General Requirements.

4.2.8.4 This QM contains or references all the topics in section 4.2.8.4 of the TNI standards Volume 1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis*, Module 2: Quality Systems General Requirements.

4.2.8.5 The Laboratory utilizes electronic signatures in the process of certifying analytical reports. Pictures of the signatures of laboratory managers are stored in the lab's Oracle database as binary large objects (BLOBs) and are associated with the user's personnel record. This BLOB is inserted into the final Laboratory report PDF when the LIMS event is certified. Because the user has logged in to their password-secured account and the process is automated, only the signature of the manager certifying the

report can be used for indicating the data have been reviewed and authorized for release.

4.2.8.6 SOPs addressing all activities of the Laboratory including all test methods and supporting activities may be found at: https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops.

All the required topics in 4.2.8.5 (f) of the 2016 TNI standards are in or referenced in the test method SOPs.

4.3 DOCUMENT CONTROL

4.3.1 Laboratory SOP LB-001, *Protocol for Preparing Standard Operating procedures (SOPs)*, describes how SOPs are created, revised, and approved. This SOP details where the current SOPs are maintained and archived. The electronic system for maintaining the SOPs is capable of creating reports with tracked revision and effective dates.

Record archiving procedures are found in SOP LB-013, *Archiving/Retrieving Documents and Using the Document Control System*. Archived records include raw laboratory data, laboratory notebooks, final reports, administrative files, personnel records, purchase requisitions, and purchase orders. The electronic document control system allows entering new archive records, identifying archives and locations, and a check out system.

The QM is updated at a minimum on an annual basis. The official version of the QM is available for viewing by all employees at https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops.

All revisions of the QM are archived and accessible on a network drive at \\FLDEP1\DEAR\Labs\SOPs\QAPLAN\.

4.3.2 Document Approval and Issue

4.3.2.1 The procedure by which an SOP is implemented or revised is as follows:

- The technician, chemist, biologist, and/or analytical group supervisor involved in carrying out the procedure prepares a draft SOP in the form of a Word document. For a revised SOP, Word's 'track changes' function is utilized to indicate the content altered during the revision.

- The draft SOP is reviewed by the Environmental Manager (EM) or Environmental Administrator (EA) in charge and submitted to the QA Officer (or delegate) as a final SOP. If a revised SOP is submitted, the EM or EA will indicate whether the change is a minor or major revision. Minor revisions are those which do not involve modifications to the method, while major revisions indicate the method has been altered significantly. A change in procedure that produces results that are incomparable with those reported before the method was modified would also justify a major revision. All revised SOPs must contain an Appendix of Significant Changes made during the revision period. The Appendix must include

the date of any significant edits and should indicate the pertinent SOP sections that have been edited.

- The QA Officer (or delegate) posts the final SOP to the Laboratory's internet site in 'portable document format' (PDF). The name of the person authorizing the SOP (supervisor submitting the final version), the effective date, and the revision date are recorded using the SOP Update Utility module of the Laboratory Information Management System (LIMS). The SOP expiration date will be set one year from the date the version was revised.

Note: In cases where a specific SOP version has been certified and subsequently undergoes a major revision, additional steps are required. The supervisor submitting the revision must also submit a method validation package and the appropriate paperwork for requesting NELAP certification of the new SOP version. ***Supervisors are responsible for ensuring that analysts are trained on new or revised SOPs and that former printed versions of SOPs are replaced with new versions. The only official versions of SOPs are those that reside on the Laboratory's internet site for SOPs. Printed copies are not considered by the Laboratory to be official SOPs.***

4.3.2.2 Revisions to the QM are submitted by the technician, chemist, biologist, and/or analytical group supervisor involved in carrying out the procedure. The proposed revisions are reviewed by the Environmental Manager/Environmental Administrator and, if acceptable, forwarded to the QA Officer. The QA Officer evaluates the changes for compliance with Laboratory policies and procedures and quality assurance issues and then is responsible for posting the revised manual.

4.4 REVIEW OF REQUESTS, TENDERS, AND CONTRACTS

4.4.1 Contract/order review is an integral part of the DEP Laboratory. All contracts/orders are reviewed and accepted only if the requirements are clear and understood, and the Laboratory has the capability and capacity to meet full customer expectations. The criteria used to review and accept projects are described in SOP LB-033, *Procedure for Receiving and Accepting Laboratory Projects*. Upon receiving a request from a client the DEP Project Manager obtains specific project information. The information includes but is not limited to the following:

- The project description (and purpose if needed)
- The analyses requested
- The sample matrices
- The number/frequency of the samples
- Completion expectations

The DEP Project Manager disseminates the information to the Laboratory Program Administrators for evaluation. For contracts with external clients, if the DEP Laboratory can

accept the work then the DEP Project Manager provides the following information in writing (or by e-mail) to the client:

- A list of the analytical methods the DEP Lab will use
- Information on whether the DEP Lab has DOH certification for the methods
- The detection limits and quantitation limits for the methods
- The costs of the analyses (if applicable)
- Additional information upon request, such as non-NELAP proficiency studies and quality assurance/control information

Once the client and the Lab mutually agree upon the project then the DEP Project Manager obtains the account information.

4.4.2 Records of reviews, including any significant changes, are maintained.

4.4.3 Communications are maintained with the client from request/quote through commencement and completion of work. This includes informing the client of any deviation from the contract or agreement.

4.5 SUBCONTRACTING OF ENVIRONMENTAL TESTS

Samples that need to be sent out to an overflow contract laboratory will show transfer to an overflow lab in the LIMS custody record unless they are sent directly from the field to the contract laboratory. For all overflow analyses except microbiology, there is a task assignment number (e.g. SA034) documented on a task assignment form, Figure 4.4. The task assignment form includes the DEP Contract Manager's signature authorizing the work, a list of sample IDs and requested analyses with turnaround time, the date/time the samples were sent out, cost information, and the identity of the custodian responsible. Samples, along with copies of the field information and the task assignment form, are delivered to the contract laboratory. The delivery person and the recipient at the contract laboratory must sign the task assignment form indicating the transfer date and time. The task assignment form becomes part of the custody record.

See SOP LB-008, *Outsourcing Analyses through a Contract Laboratory*, for further details.

4.6 PURCHASING SERVICES AND SUPPLIES

4.6.1 A list of state approved suppliers for the purchase of supplies and services is maintained by the Florida Department of Management Services (DMS) at http://www.dms.myflorida.com/business_operations/state_purchasing/myfloridamarketplace/mfmp_vendors .

The Laboratory maintains an inventory list of chemicals and supplies commonly used for analyses performed in the Laboratory. See SOP LB-030, *Purchasing and Receiving Laboratory Chemicals and Supplies*. This SOP includes procedures ensuring the necessary quality of the

purchase, checking that the proper quality was received, and how the supplies are stored if needed to maintain the quality.

4.6.2 Upon arrival at the Laboratory, purchased supplies and consumable materials are checked to ensure that they match the quality and quantity of items specified in the purchase order. Records of all purchase orders are stored and archived at the MyFloridaMarketplace web portal (https://buyer.myfloridamarketplace.com) maintained by the State of Florida.

4.6.3 The quality of items being ordered is specified prior to the purchase. This applies to the specifications of durable goods such as laboratory instrumentation and software. Similarly, the Laboratory orders consumables such as chemical reagents of known quality (purity) from reputable vendors. The quality of the chemical is usually specified by "grades" that conform to industry standards prior to their purchase. Examples include the American Chemical Society (ACS) Reagent Grade chemicals, Trace Metal Grade (TMG) acids, HPLC Grade organic solvents, Ultra High Purity (UHP) Grade gases, etc.

4.6.4 If a chemical or consumable ordered by the Laboratory is found to be lacking in the minimum quality required for its intended use, then the Laboratory will pursue the purchase of the desired item from an alternative supplier that meets the required specifications and is listed in the Florida DMS database of state approved vendors. The list is maintained at: http://www.dms.myflorida.com/business_operations/state_purchasing/vendor_information

4.7 SERVICES TO THE CLIENT

4.7.1 The DEP Laboratory strives to meet its clients' needs, including:

- Affording customers access to the Laboratory to witness testing when requested.
- Preparing, packaging, and dispatching test items and reports as required by our customers for verification purposes.
- Advising, guiding, and communicating with our customers on technical matters and providing interpretations for testing performed or to be performed in the laboratory.
- Communicating to our customers any major deviations in testing being performed. See SOP LB-002, *Non-conformance Reporting System*.
- Communicating to customers any delays that may result in the customers not receiving their test results in a timely manner.
- Notifying customers of any event that casts doubt onto the validity of results supplied to them.

4.7.2 The Laboratory solicits feedback from its customers using a comprehensive written survey once a year. Feedback from our clients by other channels such as phone and email is encouraged throughout the year to improve our operations. Feedback from Laboratory customers is maintained by the QA officer.

4.8 COMPLAINTS

The Laboratory is committed to resolving complaints and implementing suggestions for improvement. All informal complaints, suggestions, or requests for information are directed to the appropriate supervisor for resolution. If immediate resolution cannot be attained, the matter is submitted to the Program Administrator who may investigate and direct the resolution. Formal written complaints are logged with the Program and, after investigation and resolution, are responded to in writing. Copies of responses are organized and filed by the Quality Assurance officer for reference.

4.9 CONTROL OF NON-CONFORMING ENVIRONMENTAL TEST WORK

(See SOP LB-002, *Non-conformance Reporting System*).

4.9.1 Significant deviations from the Laboratory's policies and procedures, as outlined in the Quality Manual and SOPs, are not approved without appropriate documentation. Significant deviations from standard policies or practices of the Laboratory are reported to the client and documented with the analytical reports. Any samples that are prepared or analyzed beyond accepted holding times have a statement automatically stamped with the data alerting the client to the fact that tests were conducted after the samples had expired. Similarly, the failure of any quality control checks is commented with the data, directing the client to the Quality Control Report for details of the failures. Appropriate result qualifiers are also added to results for quality control check failures according to SOP LB-027, *Reporting Qualified Data and Correcting Quality Control Problems*.

4.9.2 Where non-conformances are indicative of systematic errors, the corrective action procedures described in section 4.11 are instituted.

4.10 IMPROVEMENT

The Laboratory is committed to continually improving the quality management system by:

- Multi-tier and electronic data review process (see SOP LB-025, *Event Level Authorization Checklist* and SOP LB-026, *Job Level Authorization Checklist*)
- Internal and external audits
- Systematically evaluating quality data and updating acceptance criteria
- Participating in round robins and inter-laboratory comparisons
- Performing quality system management reviews (see SOP LB-010, *Quality System Management Review*)
- Making changes to the Laboratory's capacity, capabilities, and services based on feedback from clients.

4.11 CORRECTIVE ACTION

4.11.1 General

Corrective actions for the Chemistry Program are described in the method SOPs. A list of method SOPs sorted by subsection or category can be found at https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops.

Corrective actions and notification protocols for the Biology Program are listed in Table 4.1 and/or the method SOPs. Corrective actions for taxonomy are described in the laboratory Quality Control SOPs, IZ-40, IZ-13, and AB-14. Corrective actions for microbiology, BOD, chlorophylls, and molecular are described in their respective method SOPs.

Corrective actions are initiated based on either internal QC checks, data validation by a reviewing authority, or performance audits. Outside sources such as performance evaluation studies, split samples, as well as recommendations by the DEP QA Officer may initiate corrective actions. See SOP LB-002, *Non-Conformance Reporting System*, for additional information on initiating corrective actions.

4.11.2 Cause Analysis

All non-conformances are evaluated to determine the root cause. Many factors are taken into consideration in this evaluation and the cause may or may not be directly attributable to Laboratory operations. Non-conformance causes, where identified, are documented in non-conformance reports and stored within the LIMS. Where necessary, re-training and/or changes to SOPs are implemented to address controllable errors. Details are described in SOP LB-027, *Reporting Qualified Data and Correcting Quality Control Problems.*

4.11.3 Selection and Implementation of Corrective Actions

The details of identifying corrective actions and remedies taken are detailed in SOP LB-027. The likely causes of a given problem are first identified and then corrective actions put into place to alleviate the problem. The extent of the corrective actions required is evaluated against the seriousness of the non-conformance. All corrective actions are administered within a reasonable time frame.

4.11.4 Monitoring

All corrective actions are documented and monitored to ensure compliance with the Laboratory's policy and procedures. The Laboratory QA officer maintains a list of corrective actions undertaken by Lab personnel.

4.11.5 Additional Audits

The efficacy of any corrective action is evaluated during routine internal and performance audits. Additional audits are scheduled to address non-conformances that will not allow the Laboratory to meet their established operating protocols.

4.11.6 All actions taken under this section are documented.

4.12 PREVENTIVE ACTION

4.12.1 Preventive action is a proactive process, used to identify process and quality system improvement opportunities (see for example, SOP LB-010, *Quality System Management Review*). Routine lab procedures are listed in Table 4.2, *Preventive Maintenance – Biology*, and in the individual operational SOPs. They list the types of analytical equipment utilized to perform routine analyses and the frequency of preventive maintenance tasks performed to ensure data quality.

4.12.2 All maintenance or repair to equipment is documented in a laboratory notebook or in the appropriate LIMS\Laboratory Logbook. Documentation includes a description of the problem(s), work performed, date, and analyst's initials. See section 5.5.6 for details. The management system is also evaluated to institute process revisions to create a continuous improvement process. See section 4.1.6 for an explanation of the Management Review system.

4.13 CONTROL OF RECORDS

4.13.1 General

4.13.1.1 For a description of Laboratory records, see SOP LB-006, *Records Maintenance and Storage*. Records associated with QA activities including external and internal audits, certification records, and PT studies are filed in a dedicated network folder accessible to lab personnel. Older paper records, prior to 2010, are stored in a dedicated quality assurance filing cabinet.

4.13.1.2 All records are legible, accessible, and stored in a manner that will minimize loss, damage, or deterioration. The Department continues to maintain client access to electronic and paper records for a period of not less than five (5) years after the completion of the laboratory project (see SOP LB-006 and SOP LB-013 for details).

For some special projects, including some ambient monitoring projects and records related to criminal cases, laboratory records may be stored for longer periods depending on the requirements of the project.

4.13.1.3 See section 4.1.5 (c) concerning access to laboratory records and documents.

4.13.1.4 Electronic records are copied (incremental backups) onto backup servers each business night. Full backups are conducted during weekends and the files archived to DVD as needed.

The Laboratory maintains a document control system for tracking the archive process for paper records and laboratory logbooks. The document control system is incorporated into the LIMS with records stored in Oracle tables. Paper records are boxed, labeled, and submitted to the State Records Center for storage. The State Records Center assigns the boxes a tracking number that is entered into the document control system, along with a

description of the box contents, the date range of records in the box, the archival date, and the name of the submitter. When records are needed for retrieval, the document control system database is searched for the pertinent box identification number and that number is submitted to the State Records Center for retrieval.

The Office of Technology and Information Services (OTIS) maintains the Oracle database where LIMS records are stored. A complete backup of the oracle tables is exported to a password-protected server administered by OTIS. Copies of pertinent raw and processed data may be maintained in electronic and paper format. The records in the LIMS database are maintained to ensure their availability for a period of not less than five (5) years after completion of the laboratory project. Additionally, the Laboratory maintains paper copies of all client custody records. These paper records are maintained in the Laboratory and archived offsite as needed in the State Records Center. All paper records are maintained in a temperature and humidity-controlled environment and are protected by fire suppression equipment. They are automatically destroyed after ten years unless marked as permanent.

4.13.2 Technical Records

4.13.2.1 Most of the data generated by the Laboratory during the analytical testing process is in the form of electronic records. Those data consist of raw data files generated by analytical instrumentation, chromatography acquisition software, etc. as well as processed and final database records residing in the LIMS.

All raw data files, including processed chromatography data and formatted, processed instrument files are stored on servers maintained by OTIS. Those files are organized by file type and date of generation and backed up each business night. The files are archived to optical compact disk (DVD) as needed. Software and hardware systems will be maintained to ensure that raw data are available for a period of not less than five (5) years after completion of the laboratory project. Records maintained shall allow the re-creation of the calibration and test procedures and personnel responsible for the different aspects of the test procedure. See SOP LB-006, *Records Maintenance and Storage*, for complete details.

4.13.2.2 The nature and intent of all documentation are clearly established and all records are captured at the time of generation.

4.13.2.3 Entry errors on paper records are not obliterated or erased. Corrections are made by marking a line through the error so that it is legible. The marked error is initialed, dated, and a reason for the correction is annotated when the cause is not obvious or due to simple transcription errors. Access to electronic records is restricted and where possible an electronic audit trail is maintained for write access only. Where necessary, electronic records are saved as read-only files and if changes are required, another read-only file is created instead of editing and saving the original electronic record.

4.13.3 Additional Requirements

a) Documentation of Sample History

Sample Custody

The custody of a sample is defined as one of the following:

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

Routine Custody

For most projects the DEP Laboratory provides sampling containers to field personnel. The sample chain of custody begins prior to shipping empty containers to the field personnel. Prior to shipping, the lot numbers of containers are documented in the LIMS which then generates the Sampling Kit Packing List, e.g., Figure 4.5. The Packing List is printed and signed by the laboratory technician and shipped with the containers to the customer. Samples are collected by field personnel utilizing procedures identified within their field QA Plans. After collection, the samples are shipped to the Laboratory by common carrier or are hand-delivered by the field staff. See SOP LB-015, *Packing, Shipping and Tracking Sampling Kits, and* SOP HG-015, *Preparation of Sampling Kits for the Collection of Trace Level Mercury Water Samples.*

Legal Chain of Custody

For legal chain of custody samples, a chain of custody form is used in addition to, or instead of, a sample submittal form although the submittal form can also provide legal chain of custody information. See examples of the chain of custody record in Figure 4.6. For any given sampling event, custody records are kept with the other field paperwork in the event folder at all times until the analysis is complete. A copy is sent with the final report to the customer while the original is kept in the program file with the report. At the customer's request, a copy of the internal custody records (from the LIMS and laboratory log books) can also be sent. See SOP LB-023, *Maintaining the Custody and Storage of Environmental Samples in the DEP Laboratory*, for complete details.

Sample Custody Policy

See section 5.8 under Handling Samples and Test Items and SOP LB-016, *Standard Operating Procedure for Sample Receipt and Entry into the LIMS.*

Once a sample is logged in, a custody log is automatically created for that sample in the LIMS. This log tracks the sample's movement throughout the laboratory, from sample receipt to sample disposal. See an example of the Laboratory custody log in Figure 4.7. When a sample is removed from the sample storage area, the custody is

transferred from the storage area to the user. This transaction is recorded in the custody log by date, time, and user. Each LIMS user is issued a unique ID card with a bar code with their User ID. Bar code scanners are located throughout the Laboratory. When users wish to check out or transfer samples, they scan their ID card, which transfers their unique user ID to the custody record. As each sample has a bar code label, the user can check out samples by using the bar code scanner. In the event the network or LIMS is down, the user can also manually record their user ID and use a logbook for recording sample custody. When a sample is removed from the receiving area for analysis before the login process is completed, sample chain of custody is established through analyst initials and time on the field sheet.

When users are finished with samples, they must return them to their designated storage locations for check-in and secure storage. After samples have been analyzed and final analysis reports are issued to the customer, samples are either disposed of properly (see Table 4.3, *Laboratory Waste Disposal Procedures*), returned to the client, or (in the case of legal samples) stored until the client approves disposal or transfer of the samples. For routine sample disposal, the technician scans the samples in the LIMS. The sample custody record notes the date, time, and identity of the person disposing of the sample. Records of sample login, sample check-in/check-out, sample transfers between analysts, and sample disposal are recorded electronically in the LIMS custody log. All logbook records are dated and initialed by the person(s) who carries out the task. Any errors in the printed documents are struck through with a single line and marked with the date and the person's initials. Changes made to worksheets in the LIMS Preparation Worksheet Manager are tracked electronically. If the reason for the change is not obvious a comment should be added in the corrected worksheet.

Inter-laboratory Custody

See section 4.5 for a description of custody for samples sent to a sub-contract laboratory.

Laboratory Information Management System (See SOP LB-009, *Validation of LIMS Software Development or Modifications that Affect the Calculation/Assessment of Analytical Results)*

The Laboratory uses a custom Oracle based LIMS using client-server technology. The main server is maintained by the OTIS. The database applications and client hardware are maintained by the Scientific Support Services Program.

To gain access to the LIMS, users must provide valid network and LIMS usernames and passwords. They are then presented with a menu containing only those functions required to perform their job duties, based on the security access level assigned to their unique username. The LIMS maintains an audit trail of any changes made to uploaded data. Changes are documented by the person's name and dated automatically in the LIMS records. When all the jobs within a LIMS event are

authorized for release, the event analysis report is reviewed and certified in LIMS (see SOP LB-025, *Event Level Authorization Checklist*). The review process is described in section 5.10.2.

The LIMS software is modified on a continuing basis by the Laboratory's Support Program. Revisions of the code are documented with each application. Requests for code changes, additional functionality, or interface enhancements are logged in to a LIMS Help Desk module or made via EMail. They are prioritized according to the potential for interference with data integrity or workload efficiency. Resolutions to each help desk case are documented and stored in the Help Desk data tables. See SOP LB-009, *Validation of LIMS Software Development or Modifications that Affect the Calculation/Assessment of Analytical Results.*

b) Laboratory records are maintained to ensure their availability for a minimum of five (5) years after completion of the laboratory project.

c) Records are made available to the accreditation body.

d) SOP LB-006, *Standard Operating procedures for Records Maintenance and Storage*, clarifies that software and hardware systems are maintained to ensure that raw data are available for a period of not less than five (5) years after completion of the laboratory project.

e) Procedures for accessing archived records are in SOP LB-013, *Standard Operating Procedure for Archiving/Retrieving Documents*.

f) Copies of pertinent raw and processed data are maintained in electronic and/or paper format. Additionally, the Laboratory maintains paper copies of client custody records. Records retained include:

- A test method description and reference Sample ID
- Instrument identification and a reference to operating conditions
- A reference to the method SOP describing calculations on the raw data, verification of reported results, and QC assessment
- Method performance and quality control expectations
- Software security, documentation, and assessment
- Analysts signatures, initials, or electronic identification
- Documentation to support all aspects of sample handling to include preparation, cleanup, incubation periods, weights, and instrument readouts
- Test results and record of responsible parties for laboratory records
- Documentation supporting reagent and standard history
- Calibration and calibration acceptance criteria

- Proficiency Test Results
- Record of demonstration of capability for all analysts

g) All handwritten records are recorded in permanent ink and any errors in the documents are struck through with a single line and marked with the person's initials and the date. If the reason for the correction is not obvious an explanatory comment is provided.

h) In the event that the Laboratory ceases operation, all records will be turned over to the Department's Chief Information Officer and all clients will be notified. The Department continues to maintain client access to electronic and paper records for a period of at least five (5) years after the completion of the laboratory project.

4.14 INTERNAL AUDITS

Internal system audits of the laboratory systems are conducted as described below. In addition, internal performance audits are initiated to help resolve problems and confirm the efficacy of the testing system. System audits of overflow laboratories are conducted following the pattern of the internal system audits.

4.14.1 The Laboratory Quality Assurance Officer conducts internal system audits on select laboratory systems. These internal audit procedures follow these general guidelines:

- Selected systems are audited annually.
- The QA Officer conducts the audits.
- The audit consists of the random selection of a previously reported sample project, tracking of these samples through the system, evaluation of sample results, and a follow-up laboratory audit.
- System components to be audited include, but are not limited to:

    (i) All documentation associated with sample and data handling, including linkage mechanisms employed between all records for tracking documentation for any sample datum.

    (ii) Use of established, approved procedures as outlined in this QM

    (iii) Proper execution of established procedures.

    (iv) Sample and data handling activities including:

        [a] All sample log-in, trafficking, and log-out

        [b] Sample preparations

        [c] Method calibrations

        [d] Sample analyses

        [e] Data reduction, validation, and reporting

[f] Preventive maintenance and repair procedures

[g] Standard and reagent preparations and storage

[h] Sample and waste disposal

[i] Container and labware decontamination

[j] QC management practices and assessment of analytical precision, accuracy, and sensitivity.

4.14.2 Examples of typical audit checklists can be downloaded from the website of the Florida Department of Health's Environmental Laboratory Certification Program and from the TNI website. A report is completed identifying deficiencies and corrective actions to be taken.

4.14.3 Deficiency lists and associated corrective action orders are formally promulgated to responsible staff. Corrective actions are taken in a timely manner and all customers are notified in writing if the laboratory results were impacted.

4.14.4 Subsequent checks are made to verify the implementation and effectiveness of the corrective actions. Details are provided in section 4.11.

4.14.5 Additional items:

- The Laboratory notifies clients immediately upon the identification of the need for corrective actions that affected the generated data.
- Management ensures that effective corrective actions have been instituted within the agreed upon time frame.
- Internal audits as described in this section are conducted annually.

4.15 MANAGEMENT REVIEWS

4.15.1 Management reviews are conducted according to SOP LB-010 , *Quality System Management Review*. The Quality Assurance Officer prepares a report summarizing the completion of items 4.14.1 through 4.14.5 including the completion date and responsible personnel for each of the activities. This report includes a summary of assessments by external bodies, the results of inter-laboratory comparisons or proficiency tests, QC activities, corrective or preventive actions, staffing issues, and any relevant client feedback or complaints.

4.15.2 Performance reports are generated monthly, semi-annually, and annually to track workload performance, efficiency, and spending. The reports are maintained by the Laboratory and disseminated to Laboratory supervisors.

4.15.3 The Quality Assurance Officer prepares a Quality System Management Review report on an annual basis.

4.16 DATA INTEGRITY INVESTIGATIONS

See section 5.2.7 for a description of the data integrity program. All investigations are conducted in a confidential manner. Investigations are documented and affected clients are notified.

5.0 TECHNICAL REQUIREMENTS

5.1 GENERAL

5.1.1 The quality system and technical requirements of tests and methods performed in the Laboratory conform to the requirements of the 2016 TNI standard, except where stated otherwise.

The Laboratory recognizes that many factors affect the correctness and reliability of the tests that the Laboratory performs, including:

- human factors
- accommodation and environmental conditions
- test methods and validation
- equipment maintenance and calibration
- measurement traceability
- sampling
- handling of test items

5.1.2 The Laboratory takes into account these factors in developing test procedures, personnel training, and equipment selections.

5.2 PERSONNEL

5.2.1 All Laboratory personnel are required to maintain SOPs that pertain to the work they perform within the Laboratory, and Laboratory analysts must perform initial and continuing demonstrations of proficiency according to section 4.1.5 (g).

Qualifications for personnel performing specific tasks are based on education, experience, and training procedures. All personnel must meet established minimum requirements to perform their assigned tasks of performing tests, evaluating results, and certifying results. Personnel do not perform tests unsupervised without passing minimum training requirements. Position descriptions (PDs) are maintained for each position and contain the minimum qualifications required for employment (see section 5.2.4).

Managers responsible for interpreting results are knowledgeable of the test procedures, the intent of their use and typical interferences, requirements for their use, and the significance of deviations from accepted protocols.

5.2.2 Personnel training is conducted according to SOP LB-011, *Laboratory Training System and Records Management*. All analysts and technicians engaged in analytical work are required to complete training in the methodological requirements for assigned analyses on an annual basis.

5.2.3 All tests performed by the DEP Laboratory are conducted by personnel employed by the Florida Department of Environmental Protection. Procedures for subcontracting environmental tests are provided in section 4.5.

5.2.4 Job descriptions are maintained for each position within the Laboratory. Summaries of the responsibilities of the Laboratory supervisors/managers may be found in section 4.2 of this manual.

The job/position descriptions include, where appropriate:

- Planning and performing tests.
- Evaluation of test results.
- Reporting opinions and interpretations.
- Method modification and development and validation of new methods.
- Qualifications and training programs.
- Expertise and experience required.
- Managerial duties.

5.2.5 DEP management ensures the competency of all who operate equipment, perform tests, evaluate results, and sign test reports. Adequate supervision is provided for staff undergoing training. Personnel performing specific tasks are qualified on the basis of education, training, experience, and/or demonstrated skills, as required. See position descriptions, personnel files, SOP LB-011, *Laboratory Training System and Records Management*, and the management descriptions in section 4.2.

5.2.6 Additional Personnel Requirements

Technical Manager Qualifications

Technical managers at the DEP Laboratory meet all the requirements of the State of Florida Department of Management Services broadband classifications and NELAC standards for education and experience.

5.2.7 Data Integrity Training

All employees of the DEP Laboratory are held to high professional ethical standards in the performance of their duties. All employees are required to read, understand, and sign an 'Ethics Statement' attesting to their commitment to honesty and integrity in performance of their duties. In addition, all employees are required to undergo annual ethics training. Improper, unethical, or illegal actions will be dealt with according to the published Administrative Directives of the Florida Department of Environmental Protection found at: https://www.fldepnet.org/publications/directive.

a) See SOP LB-012, *Code of Ethics*, for additional information.

b) The annual training includes protocols for reporting ethics issues, providing examples of ethical violations and reviewing the consequences of unethical behavior and resources where additional information can be referenced. If necessary, the training is updated each year to address current issues. Completion of the training is documented in the LIMS training module.

5.3 ACCOMMODATION AND ENVIRONMENTAL CONDITIONS

5.3.1 Environmental controls in the laboratory are appropriate for the tests being performed. Environmental conditions that can affect test results are listed in the relevant SOPs. For each area that requires a controlled environment, the conditions are documented. Environmental factors such as light, temperature, ventilation, and space are considered to allow tests to be performed safely and effectively.

5.3.2 Environmental conditions are maintained to meet test procedure requirements and are controlled so as not to invalidate test results or increase measurement uncertainty. If it is determined that test results are being adversely impacted by the test conditions, the tests are terminated, corrective actions instituted, and clients are notified of any impacted data.

5.3.3 The physical location of activities will be such that potential contamination will be minimized.

5.3.4 Access to all laboratories is restricted to authorized personnel and approved visitors. Visitors are supervised at all times.

5.3.5 All laboratory areas are maintained in a clean and orderly manner.

5.4 ENVIRONMENTAL TEST METHODS AND METHOD VALIDATION

5.4.1 Table 5.1 contains a listing of all chemistry analytes, preparative and analytical methods, matrices, accuracy and precision targets derived from LCSs or method requirements, and MDLs/PQLs. Modifications to methods in Table 5.1 are summarized in the method SOPs. Details concerning the procedures used for validating methods and determining MDLs and PQLs are described in SOP LB-007, *Procedure and Policy for Demonstration of Capability for Method, Instrument, and Laboratory Staff*.

Table 5.2 contains the listing of all biology parameters and their associated matrices, methods, and QA targets. Modifications to methods in Table 5.2 are summarized in the method SOPs.

The MDL is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from the method blank result. MDLs are determined using the method specified in the Federal Register, 40 CFR Part 136 Appendix B Revision 2, using LCSs prepared near the estimated detection limit as surrogates to estimate methodological noise for actual method blanks to directly measure methodological noise. If none of the method blanks give numerical results

for an individual analyte, method blanks are not required for the determination of the MDL. Where the possibility exists for significant systematic bias from sample preparation and handling or from the analytical determinative step (typically inorganic analyses), bias is taken into account when calculating detection limits. Published MDLs may be set higher than experimentally determined MDLs to (1) avoid observed positive interferences from matrix effects or common reagent contaminants or (2) for reporting convenience (i.e., to group common compounds with similar but slightly different experimentally determined MDLs). MDLs are determined in a suitable analyte-free matrix when possible. For certain analytes and matrices, no suitable, analyte-free matrix may be available. In those cases, MDLs are determined in the absence of any matrix, but in the presence of all preparatory reagents carried through the full preparatory and determinative steps. LOD verification procedures may be found in SOP LB-031, *Limit of Detection Verification*.

Practical Quantitation Limits (PQLs) are set at three (3) to five (5) times the reported MDL unless otherwise noted. Because PQL level checks are required, the practicality of the preparation of standards using commercial analytical mixes may dictate to some extent the reported PQL.

Except where specified in individual methods, the QA targets for all inorganic analyses are within the range of 80 - 120% for accuracy and < 20% RPD for precision, unless laboratory-generated data indicate that tighter control limits can be routinely maintained. This convention was adopted due to the fact that targets set according to historical data are usually less stringent. The organic QA targets are likewise statutory in nature, but based on statistically derived data from quality control samples. Warning and control limits for organic analyses are initially set for groups of compounds based on preliminary method validation data. When additional data are available, the QA targets may be reconsidered. All QA targets are routinely re-evaluated at least annually (and updated, if necessary) against laboratory generated data to ensure targets continue to reflect realistic, methodologically achievable goals.

The sources for these methods may be found in:

EPA

- *Methods for Chemical Analysis of Water and Wastes;* USEPA Office of Research and Development, Cincinnati, OH, 3/83; EPA 600/4-79-020.
- *Methods for the Determination of Metals in Environmental Samples*, USEPA Office of Research and Development, Washington DC, 6/91, EPA/600/4-91/010.
- *Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW-846*; USEPA Office of Solid Waste and Emergency Response, Washington, D.C.
- *Method for the Determination of Organic Compounds in Drinking Water, Supplement I*, EPA 500/4-90/020, July 1990.

- *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office, Washington, D.C., July 1993.
- *Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater*; USEPA Office of Water, Washington, D.C., 8/93.
- *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2;* USEPA Office of Water, EPA-821-R-16-006, December 2016.

APHA-AWWA-WPCF

- Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995 (designated as SM in Table 5.1).
- Standard Methods for the Examination of Water and Wastewater, online Edition (designated as SM in Table 5.1 and Table 5.2).

HRS

- Standard Operating Procedures, Laboratory Services, Florida Department of Health and Rehabilitative Services (designated HRS SOP).

DEP

- Method for Determination of Petroleum Range Organics (designated FL-PRO). Updated in 2019; see https://floridadep.gov/dear/quality-assurance/content/fl-pro-revisions. The previous version is Rev. 1, 11/1/1995, Florida Department of Environmental Protection.

Massachusetts DEP

- Method for Determination of Extractable Petroleum Hydrocarbons, 01/1998, Massachusetts Department of Environmental Protection (designated MA DEP EPH).

USGS

- Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Pesticides in Water by Graphitized Carbon-Based Solid- Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry

SOPs address all applicable aspects of the testing procedures including sample handling, transport, storage, preparation, calibration, test procedures, statistical techniques for evaluating data, and measurement uncertainty.

5.4.2 Selection of Methods

The Laboratory employs published analytical methods or methods that have been recognized to meet the needs of the client and are appropriate for the tests being conducted. Guidance will be provided by the Laboratory when there is a question about the test method to be used. The Laboratory usually notifies the client when an inappropriate method is requested. Exceptions arise when a sample is routinely analyzed by one or another closely related method. In such cases the group supervisor exercises his or her professional judgment in selecting the best method to use for the requested analyte(s) based on sample characteristics and the performance characteristics (MDL/PQL, interferences, etc.) of the available methods. For example the metals supervisor may routinely change components in water samples from the initially assigned Inductively Coupled Plasma test (W-ICP) to Inductively Coupled Plasma/Mass Spectrometry test (W-ICPMS) without notifying the client. In such cases the client is usually aware that either one or both methods could be used for reporting metals results from water samples.

Tests reporting parameters for Resource Conservation and Recovery Act (RCRA) methods in aqueous matrices have unique identifiers in the form of a suffix –R in the test name. For example, tests W-ICP and W-ICPMS are used to report total recoverable metals in support of Clean Water Act (CWA) projects, while tests W-ICP-R and W-ICPMS-R are used to report total recoverable metals in support of RCRA projects. Other examples include W-BNA and W-BNA-R, W-VOC and W-VOC-R etc.

5.4.3 When a new test method must be developed, validation procedures as developed under the QA Rule, 62-160, FAC, of the Department of Environmental Protection will be followed before it is put into use.

5.4.4 See TNI Standard Volume 1, Modules 4, 5, and 7 for the use of non-standard methods in Chemistry, Microbiology, and Toxicology, respectively.

5.4.5 See TNI Standard Volume 1, Modules 4, 5, and 7 for the validation of new methods in Chemistry, Microbiology, and Toxicology, respectively.

5.4.6 For quantitative laboratory measurements, statistical quality control measures are used within the Laboratory to estimate the uncertainty associated with analytical methods. See SOP LB-003, *Estimation of Measurement Uncertainty*, for a complete discussion.

5.4.7 Control of Data

5.4.7.1 Calculations and data transfers are evaluated by a multi-level system detailed in SOP LB-025, *Event Level Authorization Checklist* and SOP LB-026, *Job Level Authorization Checklist*.

5.4.7.2 Tracking changes to the LIMS and software used for data calculations and assessments are detailed in SOP LB-009, *Standard Operating Procedure for Validation of LIMS Software Development or Modifications that Affect the Calculation/Assessment of Analytical Results* , and SOP LB-006, *Standard Operating Procedure for Records Maintenance and Storage*. Permissions are established for all electronic records to restrict unauthorized access.

5.5 CALIBRATION REQUIREMENTS

5.5.1 All necessary equipment to perform the tests and associated calibrations for the methods in Table 5.1 are under the control of the DEP Laboratory and described in the Laboratory's SOPs.

Instrumentation utilized by the Biology Program for the determination of test parameters in Table 5.2 is described in the Biology SOPs. Calibration requirements for laboratory instruments in Biology are listed in Table 5.3 or in the SOPs.

5.5.2 The Laboratory ensures that all equipment and associated software used by the Laboratory meet the accuracy requirements and specifications of the test methods before being placed in service.

5.5.3 Supervisors ensure that all personnel have received adequate training on the use of laboratory equipment and that manufacturer's instruction manuals are easily accessible.

5.5.4 All equipment and instruments including software, where applicable, are uniquely identified.

5.5.5 Records are maintained for all equipment and associated software including:

- Identity of the piece of equipment and associated software
- Unique identifier
- Checks that equipment meet specifications
- Location of the equipment
- Manufacturer's instructions
- Calibration records
- Maintenance logs

5.5.6 All maintenance or repair to equipment is documented in laboratory notebooks or in LIMS\Laboratory Logbook. Documentation includes a description of the problem(s), work performed, date, and analyst's initials. Sample analyses' plans for instrument failure or maintenance are handled in this order: use backup instrument, delay the analysis if holding time can be met, postpone the sampling event, or send samples to the overflow laboratory.

5.5.7 Any equipment found to be unserviceable is tagged with an "Out of Service" tag if it is shared by multiple work groups or will be out of service for an extended period. If the unserviceable equipment is used only by a single work unit and the condition is deemed temporary (a service call has been made and/or the equipment is awaiting repairs by qualified technicians), then the supervisor may elect to notify staff directly rather than to tag the equipment.

5.5.8 All support equipment requiring calibration is labeled or otherwise documented to indicate that calibration has been performed, and when it is due.

5.5.9 The calibration of all instruments will be verified following instrument maintenance.

5.5.10 See the calibration procedures in the associated test SOPs that detail the type of checks and the frequency to verify continued calibration.

5.5.11 Any allowable correction factors, e.g. thermometer calibrations, which require the readout to be adjusted, will be clearly labeled and positioned for easy access by the analyst.

5.5.12 Procedures to gain access and the tracking of changes to the LIMS are addressed in section 4.13.3 (a) under Laboratory Information Management System. Only authorized personnel are allowed access to the Laboratory to avoid tampering with the instrumentation.

5.5.13 Additional Requirements and Clarifications

5.5.13.1 Support Equipment

- All support equipment is maintained in proper working order.
- For equipment that operates at a single temperature (incubators), a single point verification at that temperature is acceptable. All other thermometers must be calibrated at a minimum of two points that bracket their range of use.
- Maintenance or repair to equipment is documented in a laboratory notebook. Documentation includes a description of the problem(s), work performed, date, and analyst's initials.
- Calibration procedures for balances are found in SOP CM-011, *Gravimetric Analysis: Analytical Weight and Balance Calibration,* and the test SOPs.
- Calibration procedures for thermometers and thermocouples are found in SOP LB-035, *Calibration of Lab Thermometers using a Constant Temperature Calibration Bath*
- Calibration checks are conducted against nationally recognized standards.
- Calibrations or verifications are checked against the required specifications for the use of the equipment. If the calibration or verification results are not within the required specifications, equipment is removed from service until appropriate repairs can be conducted.
- Correction factors to be applied associated with the results of any thermometers are clearly labeled and positioned for easy access by the analysts.
- Micropipettes used in Molecular Biology are calibrated quarterly according to SOP PCR-2.4, *Calibration and Use of Mechanical Pipettes using PCS Pipette Calibration System*.
- Auto-Pipets are calibrated at least quarterly according to SOP CM-032, *Calibration of Auto-Pipettes and Dispensers using the Check & Track Software System.*

5.6 MEASUREMENT TRACEABILITY

5.6.1 This section of the ISO standard is not applicable to environmental measurements.

5.6.2 This section of the ISO standard is not applicable to environmental measurements.

5.6.3 Reference Standards and Reference Materials

5.6.3.1 Reference Standards

Standard sources, preparation frequency, storage, and traceability are detailed in the method SOPs.

5.6.3.2 Where possible, Reference Materials are traceable to NIST or EPA.

5.6.3.3 Intermediate checks

Continuing calibration checks are conducted according to the technical SOPs, https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops.

5.6.3.4 Standards are stored as specified in the method SOPs.

5.6.4 Additional Requirements and Clarifications

5.6.4.1 The Laboratory is a participant in TNI's Performance Evaluation Study. The QA Officer manages the performance testing program.

5.6.4.2 All purchased reagents and solvents are dated upon receipt. Reagents and solvents that are commonly used by multiple groups within the lab are tracked using a computerized inventory program. Table 5.4 lists the location and storage of reagents used by the chemistry and biology laboratories. Commonly used solvents, chemicals, and laboratory consumables such as gloves, pipette tips, sampling containers etc. are maintained in the central lab inventory. When the stock for any item in the inventory dips below a pre-determined threshold, the program alerts purchasing staff who maintain the inventory to order additional supplies. The preparations of laboratory standards from primary stock standards, neat standards, or reagents are documented in laboratory notebooks or the Standard Preparation Tracker module of the LIMS.

Additional documentation can be found in the relevant test SOPs and (for example) the following SOPs: SOP HG-012, *Mercury Group Standards Preparation Procedures*, SOP LC-039, *HPLC Standard Preparation*, SOP NU-041, *Reagent Preparation Procedure*, SOP NU-042, *Standard Preparation Procedure* and SOP SV-009, *BNA Standard Preparation.*

5.7 COLLECTION OF SAMPLES

The Laboratory provides sample containers (sampling kits) to its customers on request. The Chemistry Program does not provide field sampling services; however, the Biology Program does provide field sampling services. Table 5.5 lists the sampling capabilities and associated sampling equipment of the Biology Program.

5.7.1 The Biology Program follows the protocols described in the Department's Statewide SOP for Field Activities. All DEP field SOPs referenced in this document are available on the Department's Internet site, https://floridadep.gov/dear/quality-assurance/content/dep-sops. They include:

FS 1000 *General Sampling Procedures*
FS 2000 *General Aqueous Sampling*
FS 2100 *Surface Water Sampling*
FS 2200 *Groundwater Sampling*
FS 2300 *Drinking Water Sampling*
FS 2400 *Wastewater Sampling*
FS 3000 *Soil Sampling*
FS 4000 *Sediment Sampling*
FS 5000 *Waste Sampling*
FS 6000 *General Biological Tissue Sampling*
FS 7000 *General Biological Community Sampling*
FS 8100 *Contaminated Surface Sampling*
FS 8200 *Clean Sampling for Ultra-Trace Metals in Surface Waters*
BRN 1000 *Biological Reconnaissance Field Method*
LVI 1000 *Lake Vegetation Index Methods*
SCI 1000 *Stream Condition Index Methods*

Sampling details such as the choice of container materials, sample volumes, preservation techniques, and holding times for analytes are described in DEP SOP FS 1000, *General Sampling*.

5.7.2 Deviations from documented sampling procedures are documented in the field as comments on the submittal form which is part of the chain of custody for the samples. Figure 4.6 shows examples of the submittal form used during the collection of chemical and biological samples. Depending on the nature of the deviation, the deviation is recorded as a non-conformance and a non-conformance report is included with the sample report. The sample data will be suitably qualified by the Laboratory to accurately reflect the nature of the deviation.

5.7.3 Documentation procedures for recording relevant data during sampling are described in field SOP FD 1000, *Documentation Procedures*. This SOP, along with other field SOPs is located at https://floridadep.gov/dear/quality-assurance/content/dep-sops.

5.7.4 All submittal forms include the date and time of sample collection. Deviations from documented sampling procedure are documented at collection as described in section 5.7.2.

5.8 HANDLING SAMPLES AND TEST ITEMS

5.8.1 See section 4.13.3 (a), SOP LB-016, *Standard Operating Procedure for Sample Receipt and Entry into the LIMS.* All calibration standards, whether purchased or prepared are tracked using unique IDs and are not used beyond their expiration date. Samples are disposed of two weeks after reporting data except for those involved with criminal events (details are described in SOP LB-023, *Maintaining the Custody and Storage of Environmental Samples in the DEP Laboratory*.

5.8.2 See Section 4.13.3 (a) and SOP LB-023, *Maintaining the Custody and Storage of Environmental Samples in the DEP Laboratory and* SOP LB-016, *Sample Receipt and Entry into the LIMS,* for identifying samples upon receipt and movement through the Laboratory.

5.8.3 See Section 4.2.4 for procedures associated with any non-conformances that may affect the integrity of the data. See SOP LB-016, *Sample Receipt and Entry into the LIMS,* Section 3, for sample receiving and documentation of non-conformances associated with sample receipt.

5.8.4 Sample location can be tracked from most workstations in the Laboratory and can be changed if the sample is relocated. Samples are stored in a number of different areas listed below, separate from all standards and reagents. Temperature in the refrigerator and freezer storage units is monitored using a system comprised of probes, sensors, and software. Laboratory staff are notified by email or text alerts if units fall out of temperature range and samples are relocated if units fail. See SOP LB-004, *Managing Alerts from the Checkpoint Wireless Monitoring System,* for details about viewing and modifying appliance temperature requirements and responding to alerts.

(a) air conditioned room: metal samples and others not requiring refrigeration

(b) walk-in refrigerator 5: organic samples (e.g. BNA, pesticides)

(c) walk-in refrigerator 4: nutrients

(d) double wide refrigerator 6: nutrients

(e) incoming sample refrigerator: temporary storage for temperature sensitive biology samples awaiting login

(g) double door refrigerator 1: soils/sediments

(h) triple door refrigerator 7: nutrients

(i) triple door refrigerator 8: soils/sediments

(j) walk-in bio-freezer: biological tissue and other samples requiring freezing

(k) walk-in bio-refrigerator: biology samples that require refrigeration

(l) flammables storage refrigerator 9

(m) walk-in refrigerator 10: VOCs and PT samples

(n) mercury clean lab

(o) two cryogenic freezers: holds filtered molecular biology samples

5.8.5 Additional Requirements – Documentation

For both Chemistry and Biology, samples of a similar nature submitted together from one collector are aggregated into a single event. Event identification numbers are unique and have the format Customer Name -YYYY-MM-DD-xx where YYYY-MM-DD is the date the event

is created and xx is an accession number that is reset to -01 each day and incremented as events are logged in. Within each event, samples are grouped by analyses into jobs. All final review and reporting of data to submitters is event specific.

Additionally, each sample is assigned a unique sample identification number of the format LLL-YYYY-MM-DD-xx-yy where LLL-YYYY-MM-DD-xx is the job identification number and yy is an accession number between -01 and -99. LLL represents the lab location (TLH is for Tallahassee). YYYY-MM-DD represents the day the samples are logged into the LIMS. The LIMS also maintains an additional internal accession number (with bar code) for each sample. At log-in, a bar coded label corresponding to the sample's unique Laboratory identification number is printed and placed on each sample bottle.

All log-in information is cross-checked by a second log-in technician, after which, event login is authorized in the LIMS. The event folder is placed in a central location to await the final report.

Biology

The sample station, replicate number (if any), date, and analysis type form a unique identification for each sample. Each sample container is labeled with this information plus preservation type (if any) using waterproof markers. Field and laboratory sheets use the same nomenclature. Time of sampling is marked on the submittal form to document sequence of sampling. Laboratory bench sheets are filled out using pens with waterproof black ink. Data submittal forms are filled out using pens with waterproof black ink if conditions allow, or dark, soft-lead pencils if conditions are wet.

Algal Growth Potential/Limiting Nutrient Bioassays, Physical-chemical parameters, Phytoplankton, Toxicity Bioassays

Sample containers are identified with the site name, station number, replicate, date sampled, and time collected.

Chlorophyll-a, Microbiology, and BOD

Refer to SOP BB-030, *Sample Custody, Preparation Labels, and Worksheet Instructions for Bench Biology Samples*.

Molecular Biology

Refer to SOP PCR-5.0, *Sample Custody, Labels, and Worksheet Instructions for Molecular Biology Samples*.

Benthic macroinvertebrates

Sample containers are identified with the site name, station number, replicate (if applicable), date sampled, and time collected. This information is written directly on the Whirlpak bags used for holding Hester-Dendy samplers.

Periphyton

Sample containers are identified with the site name, station number, replicate (if applicable), date sampled, and time collected.

5.8.6 Sample Acceptance Policy

Samples arriving at the DEP Laboratory are evaluated at the time of receipt. The samples must meet certain requirements in order to be processed in the Laboratory. If some of the requirements are not met, the customer is notified of the discrepancy by the Receiving staff and a Non-conformance Report (NCR) is created.

The Receiving staff member inspects the samples for damage and sustained holding conditions and, if anything is improper, notes it on the Log-in Checklist. For samples with short hold analyses, the analysts may pick up the samples from the receiving area rather than wait until they are placed in the designated storage areas; the samples are checked out using the LIMS custody system directly from the receiving area. Samples that are received close to analysis expiration may be checked out prior to LIMS login by signing the field sheet. Samples must meet the following requirements or they will be subject to rejection:

- The labels and writing on the containers must be waterproof so that the containers can be correctly identified upon receipt at the lab.
- There must be a unique identifier on each container (field ID/test ID combination).
- The information on the submittal form must coincide with that on the containers. Examples of the submittal form supplied by the DEP Laboratory are given in Figure 4.6. The minimum information required includes:

  a) a unique sample location/field ID combination

  b) the date and time of sample collection

  c) the collector's name

  d) a LIMS Request ID (contains customer/project information)

  e) a sample matrix

  f) the analyses requested

- The containers must be preserved appropriately.
- The samples must be collected in the appropriate type of container.
- There must be sufficient volume for analysis.
- The samples must be delivered to the laboratory with sufficient time remaining for the Laboratory to meet analytical holding times.

If the information provided is insufficient to correctly process the samples an effort is made to reach the collector by phone. If the information cannot be obtained in a timely manner, the samples are subject to rejection.

5.8.7 Sample Receipt Protocols

5.8.7.1 At the time of receipt, log-in technicians check the temperature of the coolers. The log-in technicians verify the submittal form information against the sample bottles and any discrepancies are resolved. The pH of preserved samples is checked by technicians prior to sample login. The sample is checked for sufficient volume. Sample

integrity such as improper temperature and pH preservation, insufficient volume, leaking or broken bottles, etc., are entered into a Non-conformance report in the LIMS as well as documented on a Log-in Checklist with the log-in technician's initials. The VOC vials are checked for the presence of bubbles by analysts in the VOC laboratory. Trace level mercury water samples have special handling and custody procedures. Details of these procedures are described in SOP LB-016 and SOP HG-001.

Hazardous samples received as part of the Environmental Response Laboratory Network (ERLN) must be handled according to procedures described in the SOP ERLN-001, *Laboratory Accountability, Storage and Hazard Communications Procedures* and SOP LB-029, *Handling Perceived Threat Materials*.

5.8.7.2 See section 4.2.4 for procedures associated with non-conformances that may affect data quality.

5.8.7.3 The samples are logged into the LIMS with all the information listed above from the submittal form plus the following:

- WIN station number (if available)
- field parameter values (if available)
- work module number (if available)
- mode of sample delivery (e.g. common carrier, Federal Express, etc.) and delivery date
- field comments (if available)
- lab comments (if available)
- sample storage location in the Laboratory
- name of the log-in person is stored in LIMS automatically, with the time and date of sample log-in.
- bottle lot number (manufacturer's lot number on bottle)

Samples are assigned to analysts or technicians by generation of assignment worksheets or backlog reports as appropriate. As the samples are processed through the Laboratory, they and the individual analyses assume the following status designations automatically or when manually flagged by authorized personnel:

- **W**- awaiting preparation (i.e., digestion or extraction) = appears automatically at log-in for samples with analyses that require sample preparation
- **V**- available for analysis = appears automatically at log-in for samples that do not require sample preparation or appears when the completion of sample preparation is flagged by the technician
- **C**- analysis and data entry complete = changes from 'V' automatically when data are entered into the LIMS
- **A**- results authorized for release = changes from 'C' when data are authorized
- **X**- canceled

Sample holding times relating to sample preparation or analysis are entered automatically at sample login. The deadline is calculated by the LIMS and can be viewed or printed in a backlog report. Supervisors have the responsibility to ensure that all analyses under their supervision are prepared and analyzed within the holding times. Table 5.6 describes the list of acceptable sample containers, preservation techniques, and holding times for samples received by the laboratory. Chemists, biologists, and technicians who schedule their work priority from backlog reports have the responsibility to complete their individual work within the holding time. An example of a backlog report is given in Figure 5.1.

5.8.7.4 Copies of the submittal form and any field sheets are scanned into a computer and the file is named using the event ID. The originals of the submittal form, log-in checklist, and other related documents are filed together in an event folder labeled with the event name.

5.8.7.5 Sample custody procedures are described in section 4.13.3. Figure 4.6 shows examples of submittal forms used as transmittal forms for routine sample custody and documentation of custody. The information on the submittal form must coincide with that on the sample containers and include elements listed in section 5.8.6.

5.8.8 Legal chain of custody procedures are described in section 4.13.3.

5.8.9 Additional Requirements – Sample storage and disposal

Samples, sample fractions, and extracts are stored according to the storage instructions in the preservation tables FS 1000-4 through FS 1000-11 from DEP SOP FS 1000, *General Sampling Procedures* (https://floridadep.gov/dear/quality-assurance/content/dep-sops). The manner of storage prevents cross contamination and isolates the samples from standards, reagents, and food. Sample digestates may be stored under ambient conditions in the laboratory for analysis until they are discarded.

Completed samples with jobs authorized (checked from computer) are disposed of. Samples flagged as hazardous in the LIMS are disposed of according to Table 4.3. Nonhazardous aqueous samples are poured down the sink drain while flushing with tap water. Non-hazardous solid samples are disposed of in the garbage. Disposal of all samples is documented on the LIMS chain of custody record with the technician's name and date.

5.9 QUALITY ASSURANCE FOR ENVIRONMENTAL TESTING

5.9.1 The Laboratory has an established quality control program for monitoring the performance of test methods conducted under this manual. The types of quality control (QC) checks and the frequency at which they are performed are listed in the method or test SOPs. A batch of samples consists of 20 or fewer samples (with the exception of microbiology) that are prepared and/or analyzed in a single run. Microbiology samples are batched by day, so that all samples received and processed on a given day are in the same prep and analysis batch. Saline matrices are batched separately where the test is impacted by high conductivity samples.

The QC objectives are considered when selecting methods and in evaluating the capability of the Laboratory to handle sample loads that meet the QC objectives.

a) Calibration standards are checked against certified reference materials or other independently prepared standards where available.

b) The Laboratory is a participant in performance testing studies. See section 5.6.4.1.

c) Replicate analyses are used to evaluate precision (with the exception of microbiology). Precision is expressed by the relative percent difference (RPD) to compare duplicate samples/spikes A and B and is based on the formula:

$$\text{RPD (\%)} = \frac{|A-B|}{(A+B)} \times 200$$

Precision may be determined from duplicate authentic samples, from duplicate LCSs, or from matrix spike duplicates. Where RPDs are calculated based on matrix spike duplicates, A and B represent the raw results of the spiked sample (spike plus the background). Microbiology precision is evaluated according to Standard Methods 9020, in which the precision criteria (calculated by multiplying the mean range of the last fifteen points by 3.27) is compared to the log value range between duplicates.

d) The accuracy of the test method is assessed in terms of percent recovery for LCSs (fortified blanks) and matrix spikes to evaluate matrix impact.

Percent Recoveries for an LCS is calculated as:

$$\text{\% Recovery} = \frac{SC}{EV} \times 100$$

or for Matrix Spikes as

$$\text{\% Recovery} = \frac{SC - UC}{EV} \times 100$$

where:

SC = Concentration in the spiked sample
UC = Concentration in the unspiked sample. If the result is below the MDL for the unspiked sample, zero is used as the concentration)
EV = Expected value

5.9.2 Quality assurance targets (QATs) for each QC check are defined in terms of relative precision (P) or accuracy (A). Analyte concentrations associated with each QC check are defined as high, mid, or low, depending on what range of the calibration curve the check concentration falls.

A statistical program, written in Borland Delphi and integrated with the LIMS, handles the calculations of mean and standard deviation and also calculates warning and control limits for QC elements. QC data are uploaded from electronic QC analysis tools to the LIMS for storage. The statistical program looks at historical data and at a specified frequency, re-calculates accuracy and precision acceptance limits for a specific sample matrix, instrument type and QC element. Warning and control limits are calculated when at least seven or more data points are available.

They may be updated when:

(a) a minimum of at least 7 new data points are available;
(b) significant changes are made to the instrument or analytical method;
(c) they have not been updated in the last twelve months.

The user selects at least 7 new, or the most recently generated data points (accuracy, precision, or MDL values). The program calculates warning limits for these elements based on approximately two standard deviations from the mean and control limits based on approximately three standard deviations from the mean. In general, the Laboratory utilizes method or Laboratory defined warning and control limits for reporting data (i.e., statutory control limits). Those statutory limits may be modified utilizing statistical information collected over time. The precision and recovery data are used for the diagnosis of analytical problems. For laboratory parameters, calculated statistical control limits are used as criteria to accept or reject data only if they are more stringent than the criteria listed in Table 5.1.

The formulae used for the calculation of standard deviation, mean, upper and lower control, and warning limits are shown below. (Reference chapter 6 of "*Handbook for Analytical Quality Control in Water and Wastewater Laboratories" - EPA 600/4-79-019, March 1979*).

(a) Standard deviations are calculated based on the formula:

$$Sp = \sqrt{[\sum_{i-1}^{n} P_i^2 - (\sum_{i-1}^{n} P_i)^2 / n] / n - 1}$$

Where Sp = standard deviation of the population
n = total number of points in the population
Pi = the value for each point

(b) The mean is calculated as the average of all points:

$$\overline{P} = \frac{\sum_{i=1}^{n} P_i}{n}$$

(c) For recovery, the upper and lower control limits are based on a 99% confidence level.

$$UCL = P + t_{0.99}Sp$$
$$LCL = P - t_{0.99}Sp$$

(d) The upper and lower warning limits for recovery are based on a 95% confidence level.

$$UCL = P + t_{0.95}Sp$$
$$LCL = P - t_{0.95}Sp$$

where $t_{0.99}$ and $t_{0.95}$ are Student's t-distribution critical values for 99% and 95% confidence, respectively.

Because levels of statistical confidence vary with sample size, a fixed level of statistical confidence is employed that approximates 2 and 3 standard deviations. Those control limits are based on requirements specified in various EPA methods and in EPA's *'Handbook for Analytical Quality Control in Water and Wastewater Laboratories'*. The statistical program utilizes the Student's t-distribution, setting warning limits at 95% confidence and control limits at 99% confidence. Those Student's t values correspond approximately to 2 and 3 standard deviations for 7 collected datum points (~1.9 Sp and ~3.1 Sp, respectively). The advantage of using the Student's t-test is that control limits are based on known confidence limits regardless of the number of datum points in the population.

5.9.3 Essential Quality Control Procedures

(a) Standard Quality Controls

Standard quality controls include the following essential controls:

i) Positive and negative controls (LCSs and method blanks)

ii) Controls to evaluate the variability, repeatability of the test (replicates/duplicates)

iii) Test method accuracy (calibrations, continuing calibrations, certified reference materials, PT studies, and matrix spikes)

iv) Measures to evaluate test method capability

- Detection Limit Studies
- Determination of Quantitation Limits
- Range of applicability

<u>Method Detection Limits (MDL) and Practical Quantitation Limits (PQL)</u>

The MDL and PQL are defined and used for the same objectives in all analyses. Two MDL values are calculated for all applicable analytes, the first based on method blanks and the second based on low-level spikes. The larger of the two MDL values is set as the analyte's MDL. Details of calculations are found in the *Definition and*

Procedure for the Determination of the Method Detection Limit, Revision 2 published by the EPA.

- The MDL is defined as the minimum concentration of an analyte that can be measured by the method with 99% confidence that the measured concentration is distinguishable from method blank results in the sample matrix. The lab follows the MDL procedure described in the August 28, 2017 edition of 40 CFR part 136 Appendix B–Revision 2. The MDL procedure is not applicable to measurements where low-level spikes cannot be prepared such as pH, color, and specific conductance. The same procedure is employed for measurements that always produce a measurable analytical signal in method blanks (e.g., inorganic parameters) and those that do not (most organic parameters). MDLs are determined from a minimum of seven samples of reagent water containing all preparation reagents and carried through the preparation procedure and from a similar number of low-level reagent spikes (fortified at 1 – 4 times the estimated MDL) that are carried through the preparation procedure. Both the method blanks and the low-level spikes must be prepared on at least three separate days and analyzed on at least three independent analytical runs on separate days. If a lab has multiple identical instruments used for the same analysis, the blanks and low-level reagent spikes may be distributed among these instruments with a minimum of two replicates per instrument per run, to obtain a "common" MDL/PQL for the instruments.

  The MDL based on blanks, MDL_b is established at a level that excludes 99% of the analytical noise, consistent with the intent of 40 CFR part 136 Appendix B. The applicable Student's t critical value (corresponding to the appropriate degrees of freedom; $\alpha = 0.01$) is multiplied by the measured standard deviation of the population of method blank results. That factor is added to the average method blank value. If the average blank result is less than zero, either zero is used as the average or, if analytical interferences are suspected in playing a role in the measurements, the absolute value of the average method blank value may be used as the average. The latter option has the potential of elevating the MDL to accommodate unknown interferences and should be used with discretion. If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDL equal to the highest method blank result. This protocol, generally consistent with the intent and practice of 40 CFR part 136 Appendix B, avoids reporting method detection limits that are unrealistically low and below or within the population of method blank results.

  The MDL based on low-level spikes, MDL_s is established by analyzing 7 to 20 replicate reagent spikes fortified at 1 to 4 times the estimated MDL, per 40 CFR part 136 Appendix B. The MDL is set to the Student's t critical value (corresponding to the appropriate degrees of freedom; $\alpha = 0.01$) times the resulting standard deviation of the measured concentrations of the replicates.

The larger of the two MDL values, the first based on blanks and the second based on low-level spikes is set as the analyte's MDL.

Note: Tables 5.1 and 5.2 are updated annually so the MDLs used by the Laboratory may sometimes vary with those listed in both tables.

- The PQL is the lowest level of concentration that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. It is also the lowest calibration standard for most methods. This Laboratory sets the PQLs at 3 to 5 times the MDL depending on the method of analysis and the analyte, unless otherwise specified.

- A System Performance Check is defined as the procedure in which a standard consisting of one or more analytes is introduced into the analytical system to verify its performance (responses, peak shapes, retention times, or spectra) meets the minimum acceptable criteria. See SOP LB-031, *Limit of Detection Verification*.

  Additional details about the Laboratory's procedures for evaluating test method capability can be found in SOP LB-007, *Procedure and Policy for Demonstration of Capability for Methods, Instruments and Laboratory Staff.*

v) Ongoing Annual Verification of MDLs and PQLs

- During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples on each instrument, in separate batches, using the same spiking concentration used in the initial determination of the MDL. Ensure that at least seven spiked samples and seven method blanks are completed for the annual verification. If only one instrument is in use, a minimum of seven spikes are still required, but they may be drawn from the last two years of data collection.

- At least once every thirteen months, re-calculate MDL_s and MDL_b from the collected spiked samples and method blank results. Include data generated within the last twentyfour (24) months, but only data with the same spiking level. If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the method blank results.

- The verified MDL is the greater of the MDL_s or MDL_b. If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL. Adjust the PQL accordingly. The QC Statistics Tracking module in LIMS can now perform both initial and ongoing MDL and PQL calculations based on blank and PQL recovery data uploaded to LIMS on a routine basis.

vi) Data Reduction

A LIMS module performs sample and QC calculations (e.g., accuracy, precision, and % RSD). This module called the "QC Manager" is also used to upload sample and QC results into the LIMS data tables. Sample and QC result calculations are reduced as follows:

- Results from analyzed sample extracts or digestates are processed by the analytical instruments' PC-based data systems or by the laboratory Chromatography software, based on the method protocols in Table 5.1 and Table 5.2. These raw sample results are electronically downloaded from the analytical instrument to the QC Manager. For those instruments not interfaced to a PC, results from the instruments are manually entered into the QC Manager.

- Sample results and QC results are linked together by batch numbers which are generated by the Prep Worksheet Manager or QC Manager. Sample prep and analysis batches are always identified with their associated QC. The analyst enters pertinent sample prep/analysis data (amount sample digested or extracted, final digestate or extract volume, dilution factors, spiking level/solution used, etc.) and then signals the QC Manager to begin calculations. Examples of typical water and sediment calculations performed follow:

  For water samples: $C\ (\mu g/L) = D\ (\mu g/mL) \times V_f\ (mL) / V_i\ (L)$

  For soil/sediment samples: $C\ (\mu g/kg) = D\ (\mu g/mL) \times V_f\ (mL) / [M_s\ (kg) \times k]$

  where:

  C = Concentration of analyte in sample

  D = Concentration in extract or digestate

  V_f = Volume of extract or digestate

  V_i = Initial volume digested or extracted in L.

  M_s = Mass of sample digested or extracted

  k = Dry weight correction factor

- The resulting sample and associated QC results are reviewed by the analyst, and if deemed acceptable, are then uploaded to the LIMS. Current acceptance criteria (warning and control limits) for each QC element are stored within the QC Manager. If QC results are outside of the current Upper Control Limit (UCL) or Lower Control Limit (LCL), data are flagged as unacceptable, and the associated sample batch may then be re-submitted for re-digestion/re-extraction and/or re-analysis. Additional information may be found in the individual test SOPs.

vii) All chemical reagents and standards are procured from reputable vendors with the proper specifications (grade, purity) to ensure performance within the appropriate laboratory and test method specifications. Table 5.4 summarizes reagent storage.

viii) Selectivity is evaluated by employing method requirements and practices established by the Laboratory detailed in the test SOPs to confirm responses to the analyte. Checks used include dual column confirmation, inter-element interference checks, retention time windows, mass spectral tuning, and method blanks.

ix) All test conditions are monitored and documented where required by the method to ensure constant, consistent, and documentable conditions.

(b) The Laboratory utilizes method or Laboratory defined warning and control limits for reporting data. Those limits may be modified utilizing statistical information collected over time. The precision and recovery data are used for the diagnosis of analytical problems. For laboratory parameters, calculated statistical control limits are used as criteria to accept or reject data only if they are more stringent than the method criteria. QA targets and their use are provided in Tables 5.1 and 5.2. QC data are deemed acceptable if the following condition is met:

Lower Control Limit (LCL) ≤ QC Result ≤ Upper Control Limit (UCL)

Each analyst and/or technician is responsible for determining that the results of each analytical measurement have all associated QC measurements and that the acceptance criteria are evaluated and documented according to protocol. The analyst and/or technician is responsible for checking calculations, completing sample preparation, calibration, analysis and instrument logs, and completing all internal custody documentation. All written records and logs must be made using indelible ink and must include the analyst's signature or initials. Any corrections to written records must be made using a single strikeout of the original entry. The corrected entry must be dated and initialed by the individual making the correction. No correction fluid or obliterations may be made to the written records.

Each supervisor or workgroup designee is responsible for reviewing this work for completion and correctness prior to authorizing the individual results for release. The data verification procedures consist of all the QC validations and calculations checks discussed above. In addition, soundness of all data is evaluated by the nature of the sample, the inter-relationship among the parameters and the historical values if available, etc. Any discrepancy or inconsistency will initiate a recheck of data or reanalysis of the sample(s).

(c) The Laboratory has developed in-house methods/SOPs that are not cited in rules or regulations such as the Clean Water Act or SW-846. The methodology used to develop and validate these methods is identical to that used to validate regulatory methods. The quality control procedures described in sections 5.9.3 (a) and 5.9.3 (b) apply to in-house methods/SOPs as well.

5.10 REPORTING RESULTS

5.10.1 Test results are reported accurately, clearly, unambiguously, and objectively and contain all method required information, reporting requirements of the TNI standards, and requirements of the state of Florida QA Rule, Chapter 62-160, FAC.

5.10.2 Test reports contain all of the information required in 5.10.2 of the TNI standard.

Each supervisor or workgroup designee is responsible for authorizing the individual analysis results and samples for release. When all the samples within a job are authorized, the managers or supervisors are responsible for reviewing and authorizing the job for release. After all the jobs in an event are authorized, the LIMS automatically generates a list of reports that are ready to be reviewed and certified. The Program Administrator (or his/her designee) reviews the report in LIMS and if requested by the client, evaluates the data using a quality assessment tool, Automated Data Processing Tool (ADaPT). See SOP LB-025, *Event Level Authorization Checklist,* for complete details.

Once the review is completed, the report is certified in LIMS. After certification of non-criminal case reports, one copy of the event analysis report is printed with an electronic signature and retained, with the original submittal form, in the Laboratory. A .pdf file of the signed report is automatically created and, along with a .pdf of the sample submittal form, and any associated paperwork (e.g. reports received from a subcontract laboratory), and an ADaPT data file, transferred to an ftp directory accessible to the client. All final sample results with associated QC data are archived together in the LIMS committed database and can be retrieved in the future if necessary.

For criminal case reports, the generated printout does not have an electronic signature. The reviewing manager must sign and date two hard copies. One copy is retained by the DEP Laboratory and the second copy is mailed to the client. The Laboratory's electronic signature policy is described in section 4.2.8.5 of this manual.

If any analyses or preparations exceed sample holding time, the results are automatically qualified with a "Q" qualifier. See SOP LB-027, *Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems,* for the Laboratory data qualification policies and application of Table 1 of the DEP QA Rule, Chapter 62-160, FAC. Results associated with quality control data that are outside the acceptance criteria are qualified with a "J".

An appropriate comment is used to qualify results whenever:

1) batch or sample specific quality control results for an analyte cannot be realistically assessed (e.g., due to excessive analyte levels in a matrix spike);

2) quality control data indicate the uncertainty associated with the measurement(s) is outside acceptable limits;

3) sample matrix presents an unusual challenge to a method or instrument. The decision to qualify a result on these factors is at the discretion of the authorizing supervisor and must comply with SOP LB-027, *Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems*.

The report includes the page number and total number of pages.

5.10.3 Test Reports

5.10.3.1 Content in addition to the requirements of 5.10.2

a) Any deviations from the test method or any conditions affecting the reported results are described in the final report.

b) Any non-conformances to the procedures in this manual or to the test method are identified in a report comment or a non-conformance report. See SOP LB-002, *Non-conformance Reporting System*.

c) A quality control report including results for method blanks, laboratory control samples (accuracy and precision), matrix spikes (accuracy and precision), surrogates (accuracy), and calibration verification samples (accuracy).

d) See SOP LB-003, *Estimation of Measurement Uncertainty*, for reporting of measurement uncertainty. All reports indicate that uncertainty associated with the analytical results can be estimated from the reported quality assurance results and from published test performance acceptance criteria.

e) See section 5.10.5 below for opinions and interpretations.

f) Additional information required by specific methods and clients will either be provided in the report as deemed necessary or communicated directly to the client.

5.10.3.2 An electronic copy of the report, along with copies of the submittal form is provided to the customer or submitting agency. Sampling records and comments are limited to the submittal forms provided by the sampling party or agency to the Laboratory.

5.10.4 Calibration Certificates as addressed in ISO 17025 are not applicable to environmental testing.

5.10.5 Laboratory test data will be qualified according to SOP LB-027, *Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems*. Upon request, Laboratory supervisors can assist clients in interpreting data reported by the Laboratory. Such consultation will be conducted and documented where appropriate directly with the client.

5.10.6 Analyses performed by a subcontract laboratory are clearly identified on the test report. See section 4.5 for additional information.

5.10.7 Electronic Transmission of Results

Although the Laboratory may transmit data in various electronic formats to clients upon request, the Laboratory considers that only the report with a signature represents the official analysis report.

5.10.8 Report contents are uniform and designed to clearly and unambiguously present the required test information to the client.

5.10.9 Amendments to Test Reports

Required amendments to test reports will consist of a recreation of the entire report. The amended report is identified as such and the original report is referenced.

5.10.10 Exceptions

All reports are created following the same procedures. Abbreviated reports are not created for any sample analyzed by the Laboratory.

5.10.11 Additional Requirements

a) A preparation and analysis log is included with each test indicating the prep and analysis date of each sample. If the activity (preparation or sampling) has a holding time of 72 hours or less the time of the activity is included.

b) Unless otherwise noted, analytical values for soil and sediment samples are reported on a dry weight basis, and analytical values for waste and tissue samples are reported on a wet weight value. This information is provided in the remarks section of the analytical report.

c) All test components that are not accredited are identified on the test report.

d) Numeric results outside of the calibration range, where possible, are diluted and re-analyzed. In situations where this is not possible the reported results will be qualified according to established Laboratory data qualification protocols. See SOP LB-027, *Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems*.

APPENDIX A

ROLES AND RESPONSIBILITIES FOR THE CHEMICAL AGENT LABORATORY

The implementation of safety, security, and chemical hygiene procedures is the responsibility of all facility staff. The following subsections describe specific safety and chemical hygiene responsibilities for the Florida Department of Environmental Protection Laboratory's Chemical Agent Laboratory. This lab is part of the Environmental Response Laboratory Network (ERLN). It is the responsibility of all laboratory staff and their managers to know and follow the provisions of this plan. Responsibilities are listed by title.

1.1 Laboratory Director

The Laboratory Director is responsible for ensuring that this administrative practice is followed by all users of ultra-dilute chemical warfare agent (CWA) solutions and that resources and support are provided for the implementation of this plan and the requirements outlined therein. The following tasks are the responsibility of the Laboratory Director:

- Responsible for the health and safety of personnel.
- Responsible to ensure all recognized hazards are promptly addressed.
- Interact with laboratory management and personnel to ensure that the Dilute Solution Hygiene Plan (DSHP) procedures are understood and followed and assistance or resources are provided as needed.
- Serve as a back up to the Agent Manager (AM) by holding a back-up key (primary lock and key entry system) to the UDA standard storage refrigerator in case of the AM's absence.

1.2 Laboratory Manager

The Laboratory Manager (LM) is responsible for the daily operation of the CWA laboratory and daily execution of DSHP as it relates to the laboratory's activities. The LM is responsible for the health and safety of the Chemical Agent Operators (CAOs) during all UDA procedures. The LM also shares responsibilities for development, implementation, review, and support of the DSHP with the Chemical Agent Hygiene Officer (CAHO). The following tasks are the responsibility of the LM:

- Ensure that the Ultra-Dilute Agent laboratory has required safety supplies and equipment necessary to handle or store UDA materials safely.
- Ensure that UDA personnel are familiar with the Dilute Solution Hygiene Plan (DSHP) and routinely follow the requirements and procedures.
- Ensure that safety equipment is checked and ready for use.
- Request and coordinate delivery of UDA reference material from the U.S. Army Edgewood Chemical and Biological Center and Engineering Center (ECBC) with Contracting Officer's Representative (COR) or ECBC Chemical UDA Accountability Officer.

- Document all requests, coordination, and communication concerning delivery of Ultra-Dilute Agents in the Accountability Assessment log.
- Appoint a qualified CAO to perform the dry runs with dilute agents to test SOPs and approve staff readiness.
- Routinely observe CAOs performing UDA SOPs and provide recommendations in conjunction with the CAHO to improve UDA laboratory safety.
- Determine staffing, UDA laboratory access, and/or training level needs as necessary and ensure identified training levels are met by the individual.
- Conduct regular UDA inspections of housekeeping, personal protective equipment (PPE), and emergency equipment.
- Ensure that current copies of the CHP, DSHP, procedures, and other pertinent documents are readily accessible for use in the Ultra-Dilute Agent laboratory.
- Ensure that security requirements are met as specified in the Security Plan.
- Perform quarterly accountability audits with the AM as a formal witness.
- Serve as back-up for the AM for receipt of Standard Reference Materials (SRMs).
- Serve as a back-up AM for other functions.

1.3 Chemical Agent Hygiene Officer

The Chemical Agent Hygiene Officer (CAHO) is a UDA laboratory specific position and is an extension of the facility Chemical Hygiene Officer (CHO). It may or may not be the actual facility CHO. The CAHO position is held by an individual who has the knowledge and competence to develop and implement this plan, as qualified by appropriate levels of education, training, and experience. The CAHO also must demonstrate the ability to use appropriate equipment and testing procedures to anticipate, identify, and evaluate health, safety, and environmental hazards, as well as the ability to suggest means for reducing those risks. The following tasks are the responsibility of the CAHO:

- Development, implementation, review, and technical support of the DSHP in conjunction with the LM.
- Provide technical, environmental, health, and safety guidance to the LM in development and implementation of programs and procedures related to the UDA laboratories.
- Advise and assist in the improvement of Ultra-Dilute Agent laboratory safety procedures, and review and update the DSHP on an annual basis as necessary.
- Responsible for the DSHP with full authority to prepare and enforce safety policies.
- Investigate reports or situations of non-conformance with DSHP requirements.

- Prepare and/or approve UDA training materials for required visitor, CAO, responder, and remediation training levels.
- Provide and/or approve training level certifications for visitors, staff, managers, and others as appropriate for the assigned duties and level of potential exposure.
- Audit UDA laboratory functions for compliance with the DSHP, Occupational Safety and Health (OSHA) regulations, RCRA regulations and other requirements for laboratory procedures.
- Determine the level and type of personnel protective equipment (PPE) required for the various UDA procedures, conditions, audits, dry runs, and emergency response for decontamination procedures.

1.4 Agent Manager

The Agent Manager (AM) is responsible for assuring the accurate accountability of the UDA agent reference materials, from receipt and storage of the primary materials from ECBC through usage and disposal. The following tasks are the responsibility of the AM:

- Serve as the primary contact with the UDA regulatory authorities and is the team leader for compliance surveys, audits, and inspections by EPA, ECBC, or other bodies.
- Assure accurate accountability of UDA agent reference materials (primary material as received from ECBC) from receipt through disposal. Also responsible for maintaining the security and integrity of stored and in-use primary UDA solutions at all times.
- Sign courier forms for receipt of CWA material, complete the ECBC chain of custody form, and accompany the UDA solutions until they are secure in the laboratory.
- Perform checks for each working day of accountability records and housekeeping in the UDA laboratories. (Note: A “working day” is defined as any day where UDA materials are removed from secured storage.)
- Prepare monthly agent inventory reports and perform and document quarterly accountability audits.
- Serve as backup for coordinator of UDA primary solution delivery in case the LM is not available.
- Hold the keys (primary lock and key entry requirement) to the UDA standard storage refrigerator.

1.5 Chemical Agent Operators

A Chemical Agent Operator (CAO) is anyone that works directly with dilute agent solutions or unknown samples potentially containing chemical warfare agents. The CAO must be certified on the SOP under which they will be using CWA dilute solutions. The following tasks are the responsibility of the CAO:

- Perform all UDA operations using only the current and approved SOP for which operator certification has been completed.
- Conduct all operations strictly in accordance with the provisions of the DSHP, SOPs, and all applicable regulations, manuals, and directives. Any improvements or alterations must be formally approved by laboratory management before changes to the original SOP operations or procedures can be implemented.
- Observe receipt of UDA materials at the loading dock, transport of the material to the UDA laboratory, and completion of the initial entry in the UDA Accountability log.
- Document the preparation, transfer, and disposal of dilute agent standards of the Chemical Agent in the LIMS Standard Preparation Module.
- Ensure all chemical solutions are properly labeled and stored; this also includes good housekeeping practices within the work area. Responsible for maintaining the security and integrity of the UDA solutions at all times.
- Responsible for tracking the current location of all CWA dilute standards they are using. This includes documentation of transfer to other laboratories for analysis or use.
- Responsible for maintaining security for stored and in-use CWA Dilute standards at all times. Hold the numerical combination to the key pad entry system (secondary lock and key entry requirement) on the UDA standard storage refrigerator.
- Receive chemical agent orientation and safety training, and comply with the accountability procedures in addition to responsibilities under the primary CHP.
- Responsible for informing their supervisor of any factors that may compromise the safe operation of the UDA program.
- Report any accidents, incidents, hazardous conditions, or unusual circumstances to the immediate supervisor, LM, AM, or CAHO/CHO. Any event that could potentially cause or resulted in exposure or injury within the designated UDA laboratory areas must be reported.
- Use PPE required by the SOPs in the prescribed manner.

1.6 Inventory Witness

A witness is required when auditing the CWA dilute solution inventories. The witness is selected by the AM from the list of personnel with training appropriate to enter the CWA Dilute Solution Laboratory. The witness must be independent of the dilute agent operations being audited. The physical inventory witness verifies the status of the chemical inventories by signing and dating the inventory logbook.

APPENDIX B

CHEMISTRY ESSENTIAL QUALITY CONTROLS

1.0 INTRODUCTION

This section details the Quality Controls used by the Laboratory for chemical testing. Adherence to the Quality System detailed in the DEP Quality Manual will ensure that all the QC checks addressed in this appendix are being followed.

2.0 SCOPE

This appendix lists the essential quality control procedures performed by the DEP Laboratory for all testing where applicable. Additional requirements detailed in the applicable regulations are also followed.

3.0 TERMS AND DEFINITIONS

The relevant definitions from STD-ELV1-2016-Rev2.1, Section 3.0 are the preferred references. See the 2016 TNI Standard. Definitions related to this document that are used differently or do not exist in the above references are defined in the text.

4.0 METHOD SELECTION

The DEP Laboratory only uses standard methodologies (where available) acceptable to our clients and in compliance with regulatory requirements. Supporting information may be found in section 5.4 on environmental methods and method validation.

Test method quality controls, QC outlined in the test SOPs, and other requirements are followed for all tests where applicable. If no QC exists in a method employed by the Laboratory, checks are instituted from a similar method where available or, if not available, the 12 essential QC elements from 40 CFR 136.7 are applied.

5.0 METHOD VALIDATION

5.1 Validation of Methods

a) Methods are validated by performing Limit of Detection (LOD) and Limit of Quantitation (LOQ) determinations, evaluating precision and bias, and employing and achieving method criteria for checks such as mass spectral tuning and retention time windows. See SOP LB-007, *Procedure and Policy for Demonstration of Capability for Methods, Instruments and Laboratory Staff.*

b) New methods, non-standard methods, Laboratory designed methods, and method modifications are validated to confirm that the methods are fit for the intended use. The validation procedures are conducted according to SOP LB-007 and the requirements of the DEP QA Rule, Chapter 62-160, FAC.

5.2 Limit of Detection and Quantitation

Procedures are documented for each quality system matrix.

5.2.1 All sample processing and analysis steps are included in the test determination and are documented. Test methods utilized by the Laboratory will provide a LOD or MDL that meets the objectives of the analytical project.

(a) The LOD is determined for each matrix/technology/analyte by the protocol stipulated in the test method or appropriate regulation. In the absence of this information it is performed as detailed in Section 5.4 and 5.9.

(b) The LOD verification is conducted according to SOP LB-031, *Limit of Detection Verification*.

(c) An LOD study is not conducted if spiking solutions or QC samples are not available or where a detection limit is not applicable.

(d) The LOD is determined in a matrix free of interferences, where available.

(e) The LOD is verified each time there is a change in how the method is performed or when an instrumentation change impacts the sensitivity of the method.

(f) The LOD is verified quarterly using a minimum of two low-level spikes at or below the LOQ and two method blanks analyzed on each instrument during each quarter in which samples are being analyzed and results are being reported below the LOQ. The process for annual verification is described in section 5.9.3(v) on page 58 of this manual.

5.2.2 Limit of Quantitation

The established LOQ shall be the same as or above the LOD. See sections 5.4 and 5.9.3 for the methodology used for establishing the LOQ or PQL. The laboratory shall prepare and analyze a minimum of one LOQ verification sample spiked at the same concentration as the initial LOQ verification on each instrument during each quarter in which samples are being analyzed for each quality system matrix, method, and analyte.

5.2.3 Verification of Detection and Quantitation Limits

If no analysis was performed in a given year, the verification of the LOD/LOQ is not required, but a new initial LOD/LOQ verification shall be performed prior to analysis of client samples. The process for annual verification is described in section 5.9.3(v) on page 58 of this manual.

5.2.4 Documentation

At least once per year, all results of the ongoing verification sample testing are tabulated. All data representative of the current operations shall be used, if generated within the last two years. A minimum of 7 samples is required.

(a) The documentation shall include the analytical and preparation methods used, dates of preparation and testing, the batch identifiers, the testing instrument, the

quality system matrix, technology, analyte, concentration in the spiked sample with units, and the test result for each LOQ and/or DL verification test.

(b) For each analyte, documentation includes the percent recovery, the number of results (n), the mean and standard deviation of the percent recovery, and the spiking concentration of the spiked sample with units. The data can be provided to clients upon request.

5.3 Evaluation of Precision and Bias

(a) Precision and bias is evaluated according to Section 5.9.2. Initial precision targets are established from the demonstration of capability or method validation and limits may be updated as more data are generated.

(b) Procedures for assessing precision and accuracy for non-standard methods are described in section 5.9 and the QC from the SOPs associated with the individual tests. If there are variations on how the QC is assessed due to the unique nature of the tests they are discussed in the appropriate SOP. Precision and bias are evaluated against test method, client, or contractual targets and laboratory established targets. Precision and bias are evaluated over varying analyte concentrations defined as high, mid, or low, depending on what portion of the calibration curve the check concentration falls. The assessment of precision and bias is done independently for each quality system matrix and each analyte is assessed through the entire measurement system.

(c) The range of applicability is determined as detailed in section 5.9.3.

(d) Method validation protocols detailed in SOP LB-007, *Procedure and Policy for Demonstration of capability for Methods, Instruments, and Laboratory Staff* are also used for precision and bias assessments.

5.4 Evaluation of Selectivity

All analytical method checks identified in the associated test procedure SOPs are used to evaluate selectivity. These checks include, but are not limited to, mass spectral tuning, retention time windows, second column confirmation, interference checks, and method blanks.

6.0 DEMONSTRATION OF CAPABILITY

6.1 General

Demonstrations of Capability (DOC) are documented electronically as detailed in DEP Laboratory SOP LB-011, *Laboratory Training System and Records Management*. All supporting data related to the demonstration of capability is retained and accessible. Detailed procedures for establishing Initial and On-going DOCs are described in SOP LB-007.

6.2 Initial DOC

Initial demonstrations of capability are performed for all analytes and methods prior to use of the method and if there are any changes in instrument type, personnel, test method, or

anytime the test method has not been performed by the laboratory or analyst in a 12 month period.

6.2.1 Records of the initial demonstration of capability include at a minimum the requirements of section 1.6, Volume 1, Module 4 of the 2016 TNI standard.

6.2.2 Procedures for conducting the Initial Demonstration of Capability

(a) The Initial Demonstration of capability is performed as stipulated in section 1.6, STD-ELV1-2016-Rev2.1.

(b) The test is repeated for either the failed analyte(s) or all of the parameters of interest when there is a failure of one or more of the established test acceptance criteria.

(c) Repeated failures trigger corrective actions to remedy problems with the measurement system.

(d) An initial demonstration of capability is performed whenever an analyte is added to an existing accredited test method.

6.3 On-going DOC

On-going DOCs are conducted annually (at least once every 12 months) by Laboratory analysts.

6.3.1 For routine analyses that are frequently performed by experienced Laboratory analysts, the Laboratory's normal workflow for reviewing data will be used for establishing the analyst's capability. Laboratory supervisors review QC data for all routine analytical runs including the initial calibration, continuing calibration verifications, laboratory control samples, blanks, and matrix spike and surrogate recoveries. At the end of the review the supervisor signs off the analyst's bench sheets and lab report and authorized the data in the LIMS. The sign-off and authorization signify that the analyst has met all QC requirements for that method and has demonstrated the capability to perform that analysis.

6.3.2 For analyses that are performed infrequently or analysts that rarely perform the analysis (less than once per quarter), or analyses that do not have available routine QC data such as BOD and some microbiology tests, the analyst must perform or satisfy one of the following four options every 12 months.

(a) another initial DOC;

(b) a blind sample (single blind) or successful analysis of a blind performance sample;

(c) four successful consecutive laboratory QC or laboratory control samples (LCS);

(d) an authentic sample that has been analyzed by another trained analyst.

If an analyst fails to demonstrate on-going capability using the criteria listed above, then the analyst must complete a successful initial DOC to demonstrate capability. The analyst will be suspended from reporting data until the successful completion of the initial DOC.

Documentation for only one test method is maintained for similar test methods using the same technology. EPA test method 1311 (TCLP) and 1312 (SPLP) are considered similar methods differing only in the leaching solution. For some methods, it is not feasible or practical to include all analytes in the blind performance samples, LCSs, or authentic samples. If an analyst is demonstrating on-going capability using one of those samples and an analyte was not added or present in the sample, the analyte may still be reported by the analyst. Acceptability of results for analytes not added or present in ongoing capability demonstration samples shall be based on the supervisor's judgment (either using non-detection as a criterion or, if the amount is judged to be a co-contaminant, based on comparability of results produced by other experienced analysts).

7.0 TECHNICAL REQUIREMENTS

7.1. Initial Calibration

7.1.1 Calibration and standardization procedures as well as frequencies and documentation protocols for instrumentation are found in the technical SOPs, https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops. These criteria follow the requirements described in Section 1.7.1.1 of the 2016 TNI Standard, Vol. 1, Module 4.

It is the Laboratory's policy that method calibration requirements will be followed if more stringent than those described in this manual.

Protocol for Determining the Test Method Range of Applicability:

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

For regression or average response/calibration factor calculations, the minimum number of non-zero calibration points must be such that the fit preserves at least three degrees of freedom. The table below specifies the minimum number of standards to achieve this.

Type of Calibration Curve	Minimum Number of non-zero Calibration Standards
Average Response	4
Linear Fit	5

Quadratic (second order) Fit	6
Tertiary Fit	7

Laboratories may remove individual analyte calibration levels from the lowest and/or highest levels of the curve. Multiple levels may be removed, but removal of interior levels is not permitted. If one or more calibrations standards is removed, the number of standards that remain should satisfy the minimum requirements for the calibration curve fits described above. If the lowest standard of a calibration curve is removed, the reporting limit or PQL of the test will be adjusted accordingly. If the highest point is removed, the calibration range of the test is adjusted accordingly.

During the establishment of the test method range of applicability, calibration standards will be prepared and analyzed over the estimated or published range of applicability. If a linear calibration protocol is to be used, either

a) the correlation coefficient of the calibration values plotted against their respective response factors must be greater than or equal to 0.995, and

b) the relative response factors (response factor/calibration value) over the range of calibration must have a Relative Standard Deviation (%RSD) of less than or equal to 10%, or

c) the Relative Error (%RE) of at least two calibration levels, the calibration standard at the lowest level, and a standard at or close to the mid-point of the calibration curve shall meet the criteria specified in the method, or

d) the Relative Standard Error (%RSE) should meet the criterion specified in the method. If no criterion is specified in the method, the maximum allowable RSE shall be numerically identical to the requirement for RSD in the method.

The Relative Error (%RE) is calculated using the following equation:

$$\%\ Relative\ Error = \frac{x_i' - x_i}{x_i} \times 100$$

where

x_i = true value of the calibration standard, and

x_i' = measured concentration of the calibration standard

The Relative Standard Error (%RSE) is calculated using the following equation:

$$\%\ Relative\ Standard\ Error\ (RSE) = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 / (n-p)}$$

where

x_i = true value of the calibration standard, and

x_i' = measured concentration of the calibration standard

p = number of terms in the fitting equation (linear = 2, quadratic = 3) and

n = number of calibration points

If none of the above conditions are met, either the linear dynamic range must be decreased until the appropriate condition of a) and b) or c) or d) is met or a non-linear calibration protocol must be used.

Whenever a non-linear calibration protocol is utilized, a minimum of 5 calibration points must be defined for a second order fit; a third order fit requires a minimum of 6 calibration points. Measures of relative error, conditions b), c) or d) must also be satisfied for non-linear fits. When using non-linear calibration procedures, loss in sensitivity (Δ response/Δ concentration) can occur at high concentrations. To ensure that signals are not quantified in regions of poor sensitivity, control standards must be analyzed at the highest point of the nonlinear calibration curve during method validation and must meet the reference method acceptance criteria for calibration. The lower limit of the test method range of applicability is normally established at the method detection limit. The method validation includes establishment of the method detection limit and lower limit of quantitation.

For test procedures that specify calibration with a single calibration standard and a blank or zero point, the zero point and calibration standard within the linear range shall be analyzed daily to establish the slope of the calibration curve. In addition, a standard at or below the PQL shall be analyzed prior to sample analysis to verify the sensitivity of the test procedure.

7.2 Continuing calibration

Acceptance criteria for continuing calibration are outlined in the Laboratory's technical SOPs, https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops. These criteria follow the requirements described in Section 1.7.1.2 of the 2016 TNI Standard, Vol. 1, Mod. 4.

7.3 Quality Control

Quality control checks are detailed in the test SOPs and QC SOPs associated with the test type. The QC types addressed are:

7.3.1 Negative Controls

a) Method blanks are analyzed with the same procedure and test conditions as the test samples and are used to assess possible contamination during the sample preparation and processing steps. Corrective actions associated with a contaminated blank will include reprocessing the associated batch samples or qualifying all of the associated prep batch samples according to the procedures given in SOP LB-027,

Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems.

b) Method blanks are performed at a minimum of one per prep batch and consist of a quality system matrix that is similar to the associated samples that is known to be free of the analytes of interest. In instances when no readily available and economical analyte free matrix can be identified at the levels of detection required to satisfy client objectives, laboratory grade water will be used.

c) Method blanks are not applicable to certain tests.

7.3.2 Positive Controls

7.3.2.1 The LCS is taken through the entire preparation and analysis procedure and the results are compared against established acceptance criteria. Results outside of the acceptance criteria are re-analyzed or qualified according to SOP LB-027.

7.3.2.2 LCSs are performed at a minimum of one per preparation batch. LCSs are not applicable to analytes for which no spiking solutions are typically available such as total suspended solids, total dissolved solids, color, and turbidity.

7.3.2.3 The LCS is prepared by spiking a known concentration of analyte into a quality system matrix known to be free of the analyte of interest or it may be a media containing a verified concentration of the analyte. The analytes to be spiked are those specified by the test method or in the absence of this information in the method:

a) The analytes selected represents the chemistries and elution patterns of the reported components.

b) For multi-component tests the number of analytes spiked conforms to the TNI standard and the laboratory ensures that all targeted compounds are spiked over a two year period.

7.3.3 Sample Specific Controls

These controls document the effect of the matrix on the method performance and are not a measure of laboratory performance. The results of these control samples are evaluated and documented.

7.3.3.1 Matrix Spike; Matrix Spike Duplicates

a) Corrective actions for results outside of routine performance specifications include qualifying the impacted sample. See SOP LB-027.

b) The procedure for determining the spiked analytes is the same as for the LCS given in section Appendix B 7.3.2.3.

7.3.3.2 Matrix Duplicates

These are sample duplicates that are taken through the entire analytical process – except for in-bottle digestions (e.g. some low-level mercury analyses) where a sample is split into matrix duplicates after digestion. These checks are only

performed when there is a good chance that the target analyte is present. The RPD of the duplicates is calculated and compared to established acceptance criteria or method requirements.

7.3.3.3 Surrogate Spikes

Surrogates are added prior to extraction and are used for all appropriate tests. The surrogates used represent the chemistries of the targeted compounds of the method. Results are compared to method requirements and historical laboratory performance. Corrective actions include qualifying the individual samples when surrogate recoveries are outside of the established range.

7.3.4 Protocols for data reduction are in Section 5.9.3 (a) (v) and the individual test and supporting SOPs. All data reduction procedures are documented.

7.3.5 Reagent Quality, Water Quality, and Checks

(a) Reagent grade chemicals are used for all tests where the test method does not specify the reagent purity. Reagent purity requirements within the test method are followed. All purchased reagents and solvents are dated upon receipt.

(b) Water sources are monitored through the use of method blanks. Corrective actions are immediately taken when blank contamination is attributable to the water source.

(c) Titrant concentrations are verified and documented according to procedures identified in the test method SOPs.

7.3.6 Selectivity is evaluated by following all required checks within the test method and the lab test SOP.

7.4 Data Acceptance/Rejection Criteria

7.4.1 Negative Controls – Each method blank is evaluated to determine the impact on the associated sample batch. See the test method SOPs and SOP LB-027 for corrective actions and documentation associated with method blank contamination.

7.4.2 Positive Controls – Laboratory Control Samples (LCSs)

a) The results of the LCS is calculated according to Section 5.9 and compared against established acceptance criteria. The result of the calculation is documented.

b) The protocol for allowable marginal exceedances follows Section 1.7.4.2 of the 2016 TNI Standard, Vol 1, Mod. 4. Further details are provided in SOP LB-027.

7.4.3 Sample Specific controls

a) Matrix Spike; Matrix Spike Duplicate

Percent recovery from matrix spikes and relative percent difference from duplicate matrix spikes are calculated as detailed in Section 5. The results of these calculations are documented and compared against established acceptance criteria.

b) Matrix Duplicates

Precision is evaluated using the calculation for RPD in Section 5. Results are documented and compared against established acceptance criteria.

c) Surrogate Spikes

The recoveries of surrogates are calculated according to the formula given in Section 5.9. Results are documented and acceptance criteria are established based on the test method or a documented internal procedure. Results are evaluated for the effect on individual samples.

7.5 Sample Handling

a) Samples requiring thermal preservation are monitored to meet the preservation requirements referenced in Section 5.8.7 and in Table 5.6. Samples that are delivered to the Laboratory on the same day of sample collection and have not had adequate time to achieve the required temperature are considered acceptable if they are received on ice. This is documented as part of the sample receipt procedure.

b) See section 5.8.6, for the Laboratory sample acceptance policy and DEP SOP LB-016, *Sample Receipt and Entry into the LIMS*.

APPENDIX C

REFERENCES

1. "Definition and Procedure for the Determination of the Method Detection Limit-Revision 2.0", 40 CFR Part 136, Appendix B (August 2017).
2. "Nomenclature, symbols, units and their usage in spectrochemical analysis II", Spectrochim. Acta B, 33B, 242 (1978).
3. "Limit of Detection: A Closer Look at the IUPAC Definition", Analytical Chemistry 55, 712A-718 A (June 1978).
4. Handbook for Analytical Quality Control in Water and Wastewater. EPA 600/4-79-019. March 1979.
5. Methods for Chemical Analysis of Water and Wastes, USEPA Office of Research and Development, Rev. 3/83. Cincinnati, OH, 3/83; EPA 600/4-79-020.
6. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW-846; USEPA Office of Solid Waste and emergency Response, Washington, D.C.
7. Method for the Determination of Organic Compounds in Drinking Water, Supplement I, EPA 600/4-90/020, July 1990.
8. Standard Methods for the Examination of Water and Wastewater (designated SM), American Public Health Association, Washington, DC, 1995.
9. Standard Operating Procedures, Laboratory Services, Florida Department of Health and Rehabilitative Services (designated HRS SOP).
10. Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, USEPA Office of Water, Washington, D.C., 8/93.
11. Code of Federal Regulations, Title 40, Part 136; U.S. Government Printing Office, Washington, D.C., July 1993.