DIVISION OF
ENVIRONMENTAL QUALITY

Sarah Huckabee Sanders
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SECRETARY

January 9, 2024

Ms. TeAndra Taylor
U.S. EPA Region 6 Grants Team (6MD-RX)
U.S. Environmental Protection Agency
Dallas, Texas 75202-2733

RE: Quality Assurance Project Plan QTRAK-#21-216

Dear Ms. Taylor,

The Arkansas Water Quality and Compliance Monitoring Quality Assurance Project Plan (QAPP) is set to expire in March, 2024. The QAPP has recently been reviewed by Office of Water Quality personnel and it has been determined that there are no significant revisions needed to the quality assurance procedures at this time.

Office of Water Quality personnel are currently reformatting the QAPP following the recently released EPA quality assurance project plan guidance. It is anticipated that a draft document will be ready for review in early spring of this year.

Sincerely,

Jim Wise

Ecologist Coordinator
Division of Environmental Quality | Office of Water Quality
Planning Branch
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ARKANSAS WATER QUALITY
and
COMPLIANCE MONITORING
QUALITY ASSURANCE PROJECT PLAN

(QTRAK #21-216)

Expiration: March 26, 2024

DIVISION OF ENVIRONMENTAL QUALITY

Office of Water Quality

5301 Northshore Drive

North Little Rock, Arkansas 72118

The Division of Environmental Quality (DEQ) is the state's main environmental protection agency charged with protecting, enhancing, and restoring the environment for Arkansans.

2021

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Element A1: Title and Approval Sheet

ARKANSAS'S WATER QUALITY and COMPLIANCE MONITORING QUALITY ASSURANCE PROJECT PLAN

APPROVAL:

U.S. EPA Approving Official Nelly Smith /s/ Date 3/26/2021

Ms. Nelly Smith, Chief
State/Tribal Programs Section, Region 6

U.S. EPA Project Officer TeAndra Taylor/s/ Date 3/26/2021

Ms. TeAndra Taylor

ADEE QA Officer Jonathan Westmoreland Date 1/27/2021

Mr. Jonathan Westmoreland

DEQ OWQ QA Coordinator Jim Wise Date 1/27/2021

Mr. Jim Wise

ADEE Laboratory Services Manager Lessie Redican Date 1-27-2021

Ms. Lessie Redican

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Element A2: Table of Contents

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List of Abbreviations and Acronyms

ADEE	Arkansas Department of Energy and Environment
APC&EC	Arkansas Pollution Control & Ecology Commission
ARMAP	Arkansas Water Quality Monitoring and Assessment Program
ASTM	American Society of the International Association for Testing Materials.
Assessment Methodology	Assessment Methodology for the Preparation of the Integrated Water Quality Monitoring and Assessment Report
BOD	Biological Oxygen Demand
CAPA	Corrective Action and Preventive Action
CAS	Chemical Abstracts Service
cfu	Colony Forming Units
COC	Chain of Custody
COD	Chemical Oxygen Demand
COV	Coefficient of Variation
CSI	Compliance Sampling Inspections
CWA	Clean Water Act
DEQ	Division of Environmental Quality
EPA	Environmental Protection Agency. Sometimes preceded by U. S.
FSC	Field Sampling Coordinator
GCMS	Gas Chromatography-Mass Spectrometry
ICP	Inductively Coupled Plasma
ICP/MS	Inductively Coupled Plasma-Mass Spectrometry
ICP/OES	Inductively Coupled Plasma-Optical Emission Spectrometry
IT	DEQ Agency Information Technology
LCS	Laboratory Control Sample
LOQ	Limit of Quantitation
LSC	Laboratory Services Coordinator
MDL	Method Detection Limit
mg/L	milligrams per liter
MPN	Most Probable Number
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NELAC	National Environmental Laboratory Accreditation Conference
NIST	National Institute for Standards and Technology
NTU	Nephelometric Turbidity Unit
O&G	Oil and Grease
OBA	Optical Brightener Agent
OWQ	Office of Water Quality
OP	Ortho-phosphorus
PE	Performance Evaluation Sample
PT	Proficiency Testing
QA	Quality Assurance
QAC	Quality Assurance Coordinator
QAO	Quality Assurance Officer

QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
QC	Quality Control
QMP	Quality Management Plan
RCRA	Resource Conservation and Recovery Act
RWQMP	Routine Water Quality Monitoring Program
RPD	Relative Percent Difference
Rule No. 2	Regulation Establishing Water Quality Standards for Surface Waters of the Start of Arkansas. Previously known as Regulation No. 2.
RWQMN	Routine Water Quality Monitoring Network
SC	Sample Custodian
SM	Standard Methods for the Examination of Water and Wastewater
SOP	Standard Operating Procedures
SSPC	Special Study Projects Coordinator
SVOC	Semivolatile Organic Compound
SW-846	Test Methods for Evaluating Solid Waste: Physical/Chemical Methods
TKN	Total Kjeldahl Nitrogen
TNI	The NELAC Institute
TDS	Total Dissolved Solids
LIMS	Laboratory Information Management System
TMDL	Total Maximum Daily Loads
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UAA	Use Attainability Analyses
USGS	United States Geological Survey
VOC	Volatile Organic Compound
WQX	Water Quality Exchange, the US EPA data storage system

Element A3: Distribution List

The following individuals (or successor) will receive a copy of, or have access to this Quality Assurance Project Plan (QAPP):

U.S. Environmental Protection Agency (EPA)

Ms. TeAndra Taylor
Project Officer
State/Tribal Programs Section

Division of Environmental Quality (DEQ)

Office of Water Quality (OWQ)

Mr. Jim Wise
Quality Assurance Coordinator (QAC)

Mr. Jason Bolenbaugh
Field Sampling Coordinator (FSC)

Special Study Projects Coordinator (SSPC)
To be assigned as needed

Arkansas Department of Energy and Environment (ADEE),

Office of Chief Technical Officer, Laboratory Services

Mr. Jonathan Westmoreland
ADEE Quality Assurance Officer (QAO)

Ms. Lessie Redican
Laboratory Services Manager (LSM)

Element A4: Project/Task Organization

Personnel from the OWQ are responsible for collecting water quality, Compliance Sampling Inspection (CSI), sediment, toxicity, macroinvertebrate, and fish community samples. Laboratory Services will complete all chemical analyses and quality assurance of chemical analyses. OWQ and Laboratory Services personnel will perform biological analysis and its associated quality assurance, data processing, and assessment.

Quality Assurance Officer

The QAO for the project is Mr. Jonathan Westmoreland, Chemist Supervisor. Responsibilities include management and implementation of the Quality Assurance Program and the Laboratory Accreditation Program. Specific duties for this project include:

- Accreditation of laboratories.
- Annual audits of laboratory analysis procedures, equipment maintenance, and performance.
- Annual review of the QAPP.

Quality Assurance Coordinator

Mr. Jim Wise, Ecologist Coordinator, is the QAC for the OWQ. Responsibilities include:

- Overall project management.
- Ensuring all procedures and reports meet quality assurance (QA) requirements.
- Approval of sampling work plans and analytical parameters.
- Annual review of the QAPP.
- Preparing and/or updating the QAPP as needed.
- Reporting (or appointing a designee) any field quality control (QC) failures to the QAO.
- Establishing QA audits if necessary.

Field Sampling Coordinator

The FSC for the OWQ is Mr. Jason Bolenbaugh, Compliance Branch Manager. The FCS implements the ambient water sampling and compliance sampling inspection program. Responsibilities include:

- Ensuring that all field equipment and instruments meet performance and calibration criteria.
- Ensuring that proper labeling, handling, storage, and shipping requirements are met.
- Assignment and scheduling of personnel to the project.
- Selection and scheduling of all compliance sampling inspections.
- Approving all compliance sampling reports.
- Ensuring all QA procedures are attained.

Special Study Projects Coordinator

The SSPC will be identified as needed. Responsibilities include:

- Ensuring field equipment and instruments meet performance and calibration criteria.
- Ensuring proper labeling, handling, storage, and shipping requirements are met.
- Assignment and scheduling personnel to the project.
- Ensuring QA procedures are attained.

Ground Water Sampling Manager

The GSW Manager implements the Ground Water Program. Responsibilities include:

- Ensuring field equipment and instruments meet performance and calibration criteria.
- Ensuring proper labeling, handling, storage, and shipping requirements are met.
- Assignment and scheduling personnel to the project.
- Ensuring QA procedures are attained.

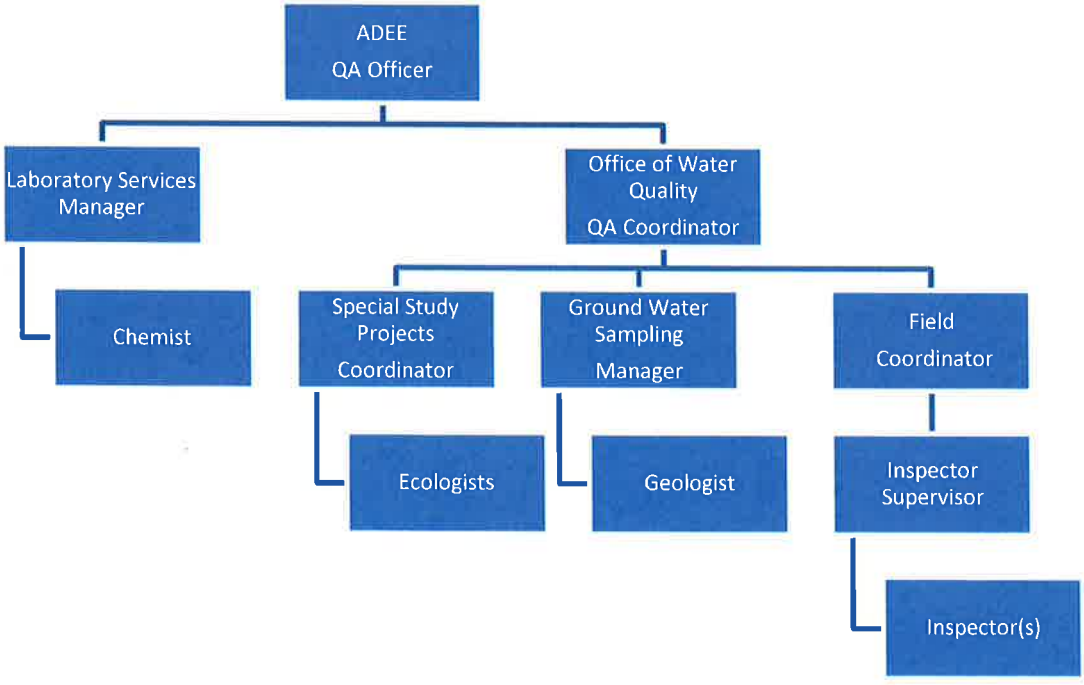
Laboratory Services Manager

The Laboratory Services Manager oversees the daily operation of the ADEE environmental laboratory. Responsibilities include:

- Ensuring laboratory functions meet QA requirements.
- Receiving consumables and perishable supplies.
- Laboratory data management.

The Project Organization chart below defines the lines of authority.

Figure 1: Project Organizational Chart



Element A5: Problem Definition/Background

Surface Water Monitoring History

The Arkansas Water Quality Monitoring and Assessment Program (ARMAP), which began in 1974, is an expansion of an earlier intrastate network. Some of the basic purposes of that monitoring network were to establish background levels and baselines of water quality, including chemical, physical and biological data, as well as seasonal and other variations. ARMAP helped establish cause and effect relationships between known point and nonpoint sources of pollution and the quality of the State's waters. ARMAP will always be vital in working towards the overall mission of the DEQ and the OWQ. In 1982, four goals were established:

- To better assess the effects of point source discharges upon water quality;
- To observe the impact of known nonpoint source discharges over the long term;
- To continue monitoring Arkansas's major rivers; and
- To monitor carefully selected, high quality (least-impaired) streams to provide long-term chemical data by physiographic region for use in future water quality standards revisions.

These four basic goals remain as the foundation of the ARMAP. However, goals are routinely revised or added to adapt to ever changing priorities to continue making progress toward achieving the overall mission of the DEQ and the OWQ. These goals are listed in the ARMAP document.

Problem Statement

Objectives of the water quality monitoring networks are to provide water quality data to determine seasonal and chronological water quality variations. Systematically collected samples over a long period of time allow for long-term trend analysis, determination of pollution control efforts, reliable assessment methods, and development of scientifically defensible water quality criteria. These data may be used by the OWQ to prioritize future, more intensive watershed water quality monitoring projects, help identify trends in water quality within the State, and to help identify waters not attaining water quality criteria.

Water Quality Monitoring

DEQ operates an integrated water quality monitoring program consisting of a Routine Water Quality Monitoring Network (RWQMN) for surface waters (lakes, rivers, and streams) and ground waters. Also, special surveys are routinely conducted on an as needed basis. The ARMAP describes these monitoring activities. In addition, monitoring point source discharges through CSIs are conducted as needed.

Element A6: Project Task Description

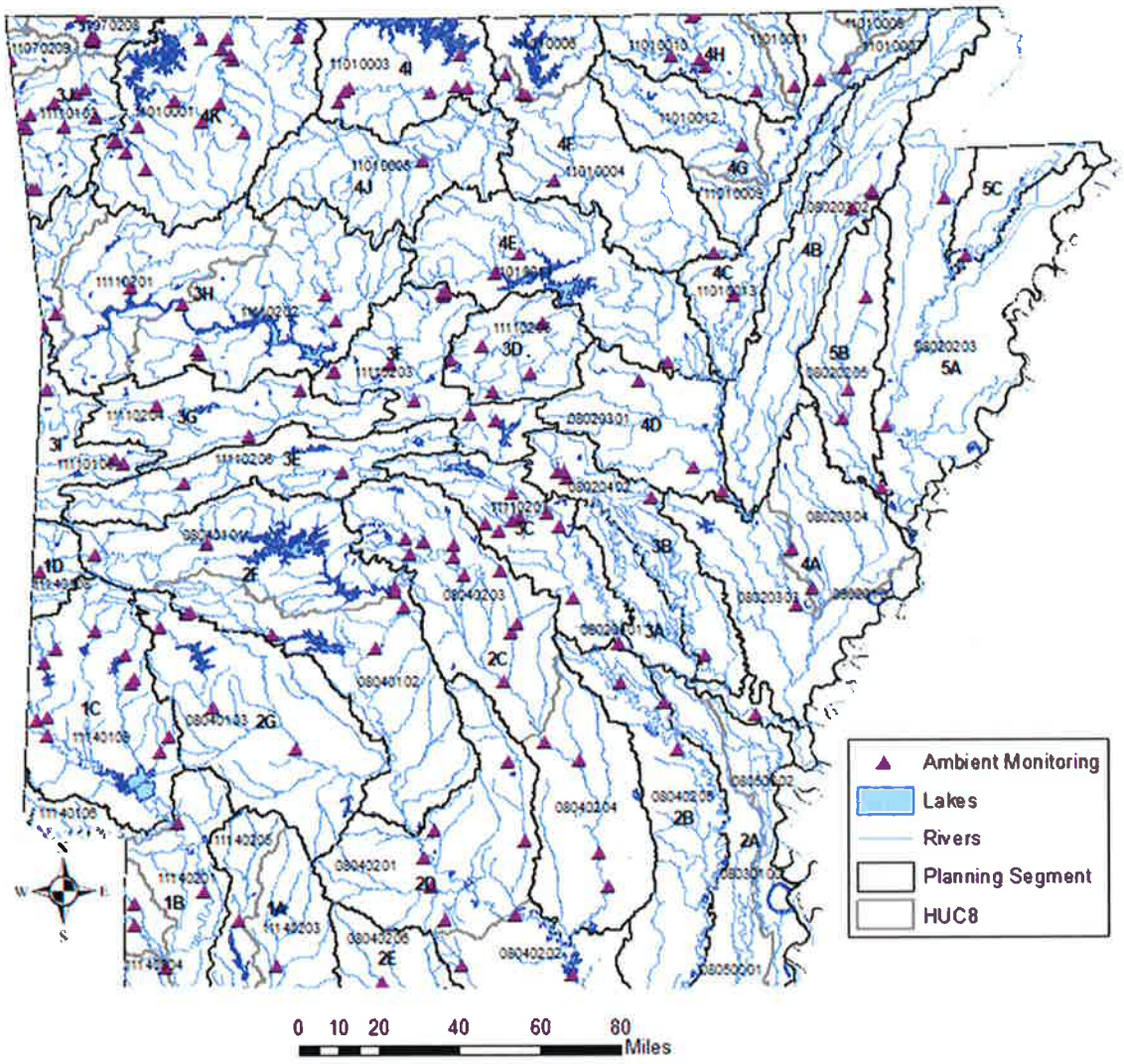
The RWQMN for surface waters consists of stations sampled monthly (Figure 2) and are analyzed for field measurements and routine water chemistry (which may include total and dissolved solids, chloride, sulfate, bacteria, nutrients, metals, minerals, and chlorophyll a). Occasionally, site specific or special analyses are performed when needed. Flow measurements are provided by the U.S. Geological Service (USGS) at select locations. Flows are either taken by continuous read gages, or wire or staff gages read monthly by USGS. Flow measurements or flow severity are taken and maintained by DEQ personnel following the DEQ flow SOP.

The RWQMN for ground waters presently consists of ten (10) monitoring areas utilizing mainly water supply wells and a lesser number of springs. Field parameters are taken at all sites, as well as oxidation-reduction potential where an undisturbed sample is possible. Parameters analyzed may differ according to location, but generally include major cations and anions, metals, nutrients, total organic carbon, and volatile and semi-volatile organic compounds.

Special study monitoring is conducted for use attainability analyses (UAA), Total Maximum Daily Loads (TMDL) support monitoring, criteria development projects, and development of assessment procedures. This monitoring is typically conducted over multiple years with field and routine water chemistry parameters collected.

CSIs are used to verify compliance with effluent limitations and to evaluate the permittee self-monitoring program.

Figure 2: Routine Water Quality Monitoring Network



Personnel

DEQ personnel perform the majority of all field duties. On occasion, personnel from other entities, mostly governmental, assist the DEQ. These individuals are identified in the work plans of the special surveys.

Quality Assurance Assessment Procedure

ADEE's QAO, or designee performs technical reviews and surveillance of field and laboratory activities to establish conformity to the DEQ Quality Management Plan.

Quality Assurance Project Plans

DEQ will develop QAPPs for special studies such as a UAA or criteria development projects as addenda to the DEQ QAPP and will document project specific data operations. No data collection will occur without a signed QAPP in place. Approved QAPPs will remain on file at the DEQ according to record retention protocol. Routine monitoring activities are covered under this QAPP.

Records Required

Field notes for field parameters measured, field equipment calibration, and any laboratory Quality Assurance/Quality Control (QA/QC) issues will be kept at the DEQ for review by the QAO until project completion.

Element A7: Data Quality Objectives for Measuring Data

The water quality monitoring program objectives are to provide water quality data for interpretation of:

- Designated use support.
- Water quality criteria attainment decisions.
- Trend analysis.
- Background or baseline water quality data establishment.
- Development and/or revision of water quality standards and criteria.

A high confidence level in the data must be attained and maintained to meet the objectives of the program. The data must also be representative of the conditions being measured and be calculated and reported in units which allow comparison of data baselines and criteria.

The data are evaluated as per the most current Assessment Methodology for the Preparation of the Integrated Water Quality Monitoring and Assessment Report (Assessment Methodology), which is based on the most current version of the Arkansas Pollution Control & Ecology Commission (APC&EC) Regulation Establishing Water Quality Standards for Surface Waters of the State of Arkansas (Rule No. 2).

Representativeness

Take measurements and samples from locations representative of the waterbody. The data quality objective is to take samples and perform analyses that depict the existing conditions as accurately as possible. The quantitative goal is to have 95% of field duplicate samples be within the acceptance criteria as outlined in Element B4.

Comparability

EPA approved analytical procedures and/or current methods from *Standard Methods for the Examination of Water and Wastewater* (SM) are used to assure data comparability.

Precision

The precision objectives are the control limits as determined by the procedures in Element B5. These control limits are based on the Relative Percent Difference (RPD) of the duplicate and spike analyses. The RPD of these analyses can be easily and quickly determined and checked against the control limit by the analyst. This allows for the immediate re-analysis of any sample determined to be "out of control" by the analyst. The quantitative goals for precision are depicted in Element B4.

Bias

Bias is the difference between the average of measurements of an analyte and its true value. A measurement is considered unbiased when the value reported does not differ from the true value. Field blanks evaluate potential bias from the process of sample handling, processing, and laboratory analysis.

Accuracy

The accuracy objectives are the control limits as determined by the procedures in Element B5, Laboratory Performance Checks. These control limits are based upon the percent recovery of spiked samples.

Completeness

Data completeness, the amount of valid data obtained compared to the amount expected, is dependent upon both field and laboratory personnel. Improper sample collection, sample contamination and out of control analytical procedures can cause data loss. The goal for completeness is to have 90% of data collected meet acceptance criteria.

Element A8: Special Training Requirements/Certifications

Laboratory

Before any analyses are performed, all laboratory personnel demonstrate proficiency on the procedures for which they are responsible. Laboratory personnel are trained under the supervision of a more senior chemist or chemist supervisor. The training process will include the analysis of QC samples with the results being checked against the normal acceptance limits.

Specific instrument training is obtained, if necessary, based on the experience of the analyst. New organic chemists will work with an experienced chemist until proficiency is demonstrated. Additional training on the other instruments will be done by repair technicians during on-site repairs. Demonstrations of proficiency are retained in electronic format in the laboratory information management system (LIMS).

Field Personnel

Field personnel are trained on proper water quality sampling, sample handling and preservation techniques, equipment usage and maintenance, and other field and in-house procedures under the supervision of senior scientist or managers. This training includes, but is not limited to, the following:

- Annual training occurs as a refresher to those methods routinely used in sampling
- Periodic training of entire field staff when new, specialized sampling techniques for unusual constituents occur
- Specialized, one-on-one field training as needed, or as soon after a problem has been identified by field reports, senior staff members, or supervisors
- Additional federal, state, or private sponsored training
- The QAO or designee performs QA/QC training of field personnel regarding the operation of field monitoring equipment and special monitoring assignments

Notes of QA/QC problems will be documented. Records of the training activities will be kept on file as per the DEQ's document retention policy, Element A9.

Element A9: Documentation and Records

Field and Laboratory Data Retention Procedures

Data, including raw data, bench sheets, QC checks, calibration logs, instruments printouts, chain of custody forms, field sheets, Standard Operating Procedures (SOP) documents, QA documents, and project reports, may be scanned in accordance with the DEQ's document retention policy as described in the Quality Management Plan (QMP). Maintain federal grant documents and associated records for a minimum of five years. Maintain laboratory documents for a minimum of seven years.

Enter water quality data into the EPA Water Quality Exchange (WQX) data storage system if the system is available. Quality Assurance of the WQX database is not the responsibility of DEQ personnel and therefore is not addressed in this QAPP. When possible, data generated are available to the public by accessing the WQX or the DEQ website.

Element B1: Sampling Process and Design

General Experimental Design

The activities of this project consist of the implementation of the most recent version of the ARMAP and any associated work plans. The ARMAP is designed to evaluate water quality and trends in the State's waters. Data from these programs are used to prepare Arkansas's Integrated Water Quality Monitoring and Assessment Report (combined Section 305(b) and Section 303(d)) and updates of the WQX.

Water Quality Constituents

Samples for water quality constituents such as bacteriological, metals, minerals, in situ measurements of water temperature, pH, conductivity, and dissolved oxygen, and biological samples such as periphyton, fish and benthic macroinvertebrates may be collected.

Sampling Network Design

The ARMAP consists of stations sampled monthly as part of the Routine Water Quality Monitoring Program (RWQMP). Other water quality monitoring sites are associated with special studies. The locations of these stations are usually described within the work plan of the study. Specific water quality constituents included in these programs are determined and usually identified in the associated work plans.

The ground water program consists of well and spring sites across the state. Parameters selected at each site are based on site-specific conditions, but usually include major cations and anions, metals, and nutrients.

Compliance Monitoring

The CSIs assess compliance with effluent limitations and evaluate the permittees' self-monitoring program. The program consists of inspecting point source dischargers as scheduled in of the current Clean Water Act (CWA) Section 106 work plan.

Element B2: Sampling Methods Requirements

Surface Waters (Chemical, Biological and Physical)

Collect and preserve samples according to the criteria in the current DEQ SOP for collection of chemical, physical and biological samples. If deviations from these procedures are necessary, record the methods used and reasons for the deviation, and the identification of the field personnel in the field sampling log book.

Ground Water Samples

Sample ground water according to recommended procedures found in the following documents in order of importance:

- EPA – Resource Conservation and Recovery Act (RCRA) Ground-Water Monitoring Technical Enforcement Guidance Document
- EPA - Handbook; Ground Water, Volume II: Methodology
- EPA - Subsurface Characterization and Monitoring Techniques; A Desk Reference Guide, Volume I: Solids and Ground Water, Appendices A and B
- USGS - National Handbook of Recommended Methods for Water-Data Acquisition

Prior to collecting a sample, domestic wells which are in current use are purged of sufficient volume to drain the holding tank(s) and associated piping. Wells installed for monitoring purposes only are purged of three well volumes or until field parameters have stabilized, a fluctuation equal to or less than the meters accuracy.

Field measurements should include temperature, specific conductance, and pH. Sample containers and the collection of field parameters should follow the procedures outlined in the current DEQ SOP.

Recording Data

Field sheets, chain-of-custody forms, and field notebooks should contain complete, unabbreviated information as outlined in the current DEQ SOP.

Element B3: Sample Handling and Custody Requirements

The purpose of the chain of custody (COC) procedure is to demonstrate the reliability of evidence by creating an accurate written record of the possession of a sample from collection to possible introduction into evidence. This procedure ensures samples are collected, transferred, stored, analyzed, and destroyed only by authorized personnel.

Custody and Storage

A COC completed as instructed in the DEQ SOP must accompany samples. A sample is in custody if it is in any one of the following states:

- In actual physical possession
- In view, after being in physical possession
- In a secure area, restricted to authorized personnel

Sample Collection – Water and Biological

- Designate one individual, when possible, to collect all water quality samples during a single outing. However, all personnel doing the sampling should be trained on the sampling procedures.
- Designate a single individual as the individual that will direct the sampling and preservation of biological samples during a single outing.
- Collect samples as instructed in the DEQ SOP.
- Complete field notes as instructed in the DEQ SOP.
- The sample collector is responsible for the care and custody of the sample(s) until they are relinquished. The sample custodian must provide proper storage conditions and ensure delivery of samples within the permitted holding times. Samples must be in physical possession of the collector in a secure area restricted to authorized personnel. The sample collector is responsible for the samples until the laboratory receives custody.

Sample Shipment and Transfer of Custody

- Obtain a bill of lading when samples are shipped by common carrier. Retain bill of lading as part of the permanent COC.
- A COC must accompany samples delivered to other personnel. This consists of "relinquished by" and "received by" printed names and signatures on the COC form.
- Deliver samples to authorized personnel. Record transfer of custody with printed names, signatures, date, and time of the transferor and transferee on COC.
- Laboratory Services personnel are authorized to receive samples in the laboratory.

Laboratory Custody

- The chemist supervisor or designee shall be the Sample Custodian (SC). The SC receiving the sample is responsible for distributing the samples to the laboratory personnel or storing the samples under the appropriate conditions. In the event of the SC's absence, a substitute is designated.

- Record samples received in the laboratory in LIMS, with the sample description, date and time collected, name of collector, date and time received, and person receiving the sample.
- Laboratory personnel are responsible for the care and custody of a sample once it is relinquished to them and should be prepared to testify that the sample was in their possession or secured in the laboratory at all times.
- The laboratory area shall be maintained as a secured area and shall be restricted to authorized personnel.
- All analyses must be completed within the approved holding times as outlined in the most current 40 C.F.R. Part 136 - Guidelines Establishing Test Procedures for the Analysis of Pollutants.
- Once sample analyses are completed, the unused portion of the sample, with identifying labels and other documentation must be returned to the laboratory supervisor for secure storage.
- Destroy samples only upon the order of the chemist supervisor, in consultation with the sampler.

Element B4: Analytical Methods Requirements

Analytical procedures are referenced in the most current "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act," 77 Federal Register 29757, 6/18/2012; 40 C.F.R Part 136 or approved EPA Methods (SW-846) or approved Standard Methods.

Table 1: Analytical Methods and Precision Requirements for Field, Lab, and Bacteriological Parameters

Parameter	CAS	Units	Method	LOQ	Field Precision RPD	LCS Recovery	MS/MSD Recovery	MS/MSD RPD
pH		Standard Units	SM 4500 - H^+B 2011 and DEQ SOP		N/A	N/A	N/A	N/A
Dissolved Oxygen		mg/L	ASTM D888-09 (C), SM 4500 - O (G) 2011, and DEQ SOP		N/A	N/A	N/A	N/A
Secchi Depth		meters	DEQ SOP		N/A	N/A	N/A	N/A
Flow		cfs	DEQ SOP		N/A	N/A	N/A	N/A
Flow Severity		0-Dry, 1-Intermittent, 2-No Flow, 3-Low Flow, 4-Typical Flow, 5-High Flow, 6-Flood	DEQ SOP		N/A	N/A	N/A	N/A
Conductivity		µmhos	SM 2510 B-2011 used in Field and DEQ SOP EPA 120.1 used in lab	1	±20%	90-110%	80-120%	±20%
Temperature		Degrees Celsius (°C)	SM 2550 B-2011 and DEQ SOP					
Turbidity		NTU	SM 2130B-2011 used in Field; EPA 180.1 used in lab	0.05	±20%	90-110%	80-120%	±20%
Total Dissolved Solids (TDS)		mg/L	SM 2540 C-2011	5	±5%	90-110%	NA	NA
Total Suspended Solids (TSS)		mg/L	SM 2540 D-2011	2	±5%	90-110%	NA	NA
Alkalinity		mg/L	EPA 310.2 Modified	6	±20%	90-110%	80-120%	±20%
E. coli		cfu/100 mL	EPA 1603					
E. coli		MPN	Colilert					
Fecal Coliform		cfu/100mL						
Fecal Coliform		MPN						
Chloride	16887-00-6	mg/L	EPA 300.0	0.500	±20%	90-110%	80-120%	±20%
Sulfate	14808-79-8	mg/L	EPA 300.0	0.500	±20%	90-110%	80-120%	±20%
Fluoride	16984-48-8	mg/L	EPA 300.0	0.100	±20%	90-110%	80-120%	±20%
Bromide	24959-67-9	mg/L	EPA 300.0	0.100	±20%	90-110%	80-120%	±20%
Biochemical Oxygen Demand (BOD)		mg/L	SM 5210 B-2011	0.20	±20%	84.5-115%	NA	NA
Carbonaceous Biochemical Oxygen Demand-5 day		mg/L	SM 5210 B-2011					
Hardness-Total as CaCO3		mg/L	SM 2340 B-2011					
Total Organic Carbon (TOC)		mg/L	SM 5310 C-2011	1.00	±20%	85-115%	80-120%	±20%

Table 1: Analytical Methods and Precision Requirements for Field, Lab, and Bacteriological Parameters

Parameter	CAS	Units	Method	LOQ	Field Precision RPD	LCS Recovery	MS/MSD Recovery	MS/MSD RPD
Ammonia as Nitrogen		mg/L	SM 4500-NH3 H-2011	0.030	±20%	80-120%	80-120%	±20%
Nitrate+Nitrite, as Nitrogen		mg/L	SM 4500 NO3- F-2011	0.050	±20%	80-120%	80-120%	±20%
Kjeldahl Nitrogen as Nitrogen		mg/L	Digestion: SM 4500-P, J-2011 Analysis: SM 4500-NO_3- F-2011	0.100	±20%	80-120%	80-120%	±20%
Ortho-phosphorus*, as phosphorus		mg/L	SM 4500-P, G-2011	0.020	±20%	80-120%	80-120%	±20%
Total Phosphorus, as phosphorus		mg/L	Digestion: SM 4500-P, J-2011 Analysis: SM 4500-P, G-2011	0.020	±20%	80-120%	80-120%	±20%
Chlorophyll a		µg/L	EPA 445.0 (modified)	0.14	±20%	NA	NA	NA
Phycocyanin		µg/L	EPA 445.0 (Modified)	20.0	±20%	NA	NA	NA

*Ortho-phosphorus (OP) is NOT field filtered using a 0.45 µm filter as specified by the method. Samples are filtered in the laboratory using a 1.1 µm filter. The OP data are used only as an indicator of water quality trends. The quality of the OP data generated is adequate for this purpose.

Metals

Analyze Total Metals after preliminary digestion using modifications of EPA 200.7, Revision 4.4 "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry," and 200.8, Revision 5.4, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry." for aqueous samples; or SW 846-3051A, "Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils" for soil samples.

Analyze Dissolved Metals after filtration at the time of collection using a 0.45micron filter followed by acidification to a pH of <2 using nitric acid.

Analyze Total and Dissolved Metals using EPA 200.8 Rev. 5.4 (ICP/MS) or EPA 200.7, Rev. 4.4(ICP/OES)

Table 2: Analytical Methods and Precision Requirements for Metals

Parameter	CAS No.	Method EPA 200.7 LOQ	Method EPA 200.8 LOQ	Field RPD Both Methods	LCS % Recovery EPA 200.7	LCS % Recovery EPA 200.8	MS/MSD% Recovery EPA 200.7	MS/MSD % Recovery EPA 200.8	MS/MSD RPD Both Methods
Aluminum	7429-90-5	0.100 mg/L	40.0 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Antimony	7440-36-0	0.100 mg/L	25.0 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Arsenic	7440-38-2	0.100 mg/L	1.00 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Barium	7440-39-3	0.010 mg/L	5.00 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Beryllium	7440-41-7	0.010 mg/L	0.500 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Cadmium	7440-43-9	0.005 mg/L	0.300 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Calcium	7440-70-2	0.500 mg/L	0.250 mg/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Chromium	7440-47-3	0.010 mg/L	2.00 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Cobalt	7440-48-4	0.020 mg/L	2.50 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%

Table 2: Analytical Methods and Precision Requirements for Metals

Parameter	CAS No.	Method EPA 200.7 LOQ	Method EPA 200.8 LOQ	Field RPD Both Methods	LCS % Recovery EPA 200.7	LCS % Recovery EPA 200.8	MS/MSD% Recovery EPA 200.7	MS/MSD % Recovery EPA 200.8	MS/MSD RPD Both Methods
Copper	7440-50-8	0.020 mg/L	3.00 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Iron	7439-89-6	0.100 mg/L	50.0 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Lead	7439-92-1	0.100 mg/L	0.500 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Magnesium	7439-95-4	0.200 mg/L	0.250 mg/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Manganese	7439-96-5	0.020 mg/L	10.0 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Nickel	7440-02-0	0.100 mg/L	20.0 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Potassium	7440-09-7	1.00 mg/L	0.250 mg/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Selenium	7782-49-2	0.100 mg/L	3.00 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Silver	7440-22-4	0.010 mg/L	0.300 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Sodium	7440-23-5	1.00 mg/L	0.250 mg/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Thallium	7440-28-0	0.100 mg/L	0.500 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Vanadium	7440-62-2	0.010 mg/L	2.50 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%
Zinc	7440-66-6	0.010 mg/L	10.0 ug/L	±20%	85-115%	85-115%	75-125%	70-130%	±20%

Volatile Organic Components

Analyze Volatile Organic Compounds either by ADEE Laboratory Services or by an Arkansas accredited commercial laboratory by GC/MS, using SW-846 Method 8260C Rev. 3, 8/2006, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry," or a more recently approved revision.

Table 3: Analytical Methods for Volatile Organic Components

Compound	CAS Number	Compound	CAS Number
Fluorobenzene(IS)	462-06-6	Bromoform	75-25-2
Chlorobenzene-d5(IS)		Styrene	100-42-5
1,4-Dichlorobenzene-d4(IS)		1-1-2-2-Tetrachloroethane	79-34-5
Dibromofluoromethane(Surr.)		o-Xylene	95-47-6
1-2-Dichloroethane-d4(Surr)		1-2-3-Trichloropropane	96-18-4
Toluene-d8(Surr.)	2037-26-5	Isopropylbenzene	98-82-8
4-Bromofluorobenzene(Surr.)	460-00-4	Bromobenzene	108-86-1
Dichlorodifluoromethane	75-71-8	n-Propylbenzene	103-65-1
Chloromethane	74-87-3	2-Chlorotoluene	95-49-8
Vinyl-Chloride	75-01-6	4-Chlorotoluene	106-43-4
Bromomethane	74-83-9	1-3-5-Trimethylbenzene	108-67-8
Chloroethane	75-00-3	tert-Butylbenzene	98-06-6
Trichlorofluoromethane	75-69-4	1-2-4-Trimethylbenzene	95-63-6
1-1-Dichloroethene	75-35-4	sec-Butylbenzene	135-98-8
Methylene_Chloride	75-09-2	1-3-Dichlorobenzene	541-73-1
trans-1-2-Dichloroethene	156-60-5	1-4-Dichlorobenzene	104-46-7
1-1-Dichloroethane	75-34-3	p-Isopropyltoluene	99-87-6
cis-1-2-Dichloroethene	156-60-5	1-2-Dichlorobenzene	95-50-1
Bromochloromethane	74-97-5	n-butylbenzene	104-51-8
Chloroform	67-66-3	1-2-Dibromo-3-chloropropane	96-12-8
2-2-Dichloropropane	590-20-7	1-2-4-Trichlorobenzene	120-82-1
1-2-Dichloroethane	107-06-2	Naphthalene	91-20-3
1-1-1-Trichloroethane	71-55-6	Hexachlorobutadiene	87-68-3
1-1-Dichloropropene	563-58-6	1-2-3-Trichlorobenzene	87-61-6
Carbon_Tetrachloride	56-23-5	Acetone	67-64-1
Benzene	71-43-2	2-Butanone	78-93-3
Dibromomethane	74-95-3	4-Methyl-2-pentanone	108-10-1
1-2-Dichloropropane	78-87-5	2-Hexanone	591-78-6
Trichloroethene	79-01-6	1-1-1-2-Tetrachloroethane	630-20-6
Bromodichloromethane	75-25-4	Chlorobenzene	108-90-7
cis-1-3-Dichloropropene	10061-01-5	Ethylbenzene	100-41-4

Table 3: Analytical Methods for Volatile Organic Components

Compound	CAS Number	Compound	CAS Number
trans-1-3-Dichloropropene	10061-02-6	1-2-Dibromoethane	106-93-4
1-1-2-Trichloroethane	79-00-5	Tetrachloroethene	127-18-4
Toluene	108-88-3	Dibromochloromethane	124-48-1
1-3-Dichloropropane	142-28-9		

Semivolatile Organic Compounds

Analyze Semivolatile organic compounds either by ADEE Laboratory Services or by an Arkansas accredited commercial laboratory by GC/MS using SW-846 Method 8270D Rev. 4, 2/2007, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry," or a more recently approved revision.

Table 4: Analytical Methods for Semivolatile Organic Compounds

Compound	CAS Number	Compound	CAS Number
1,4-Dichlorobenzene-d4 (IS)		Hexachlorobutadiene	87-68-3
Naphthalene-d8 (IS)		N-Nitrosodibutylamine	924-16-3
Acenaphthene-d10 (IS)		4-Chloro-3-methylphenol	59-50-7
Phenanthrene-d10 (IS)		2-Methylnaphthalene	91-57-6
Chrysene-d12 (IS)		Hexachlorocyclopentadiene	77-47-4
Perylene-d12 (IS)		1-2-4-5-Tetrachlorobenzene	95-94-3
Phenol-d6(Surr.)		2-4-5-Trichlorophenol	95-95-4
2-Fluorophenol(Surr.)	367-12-4	2-4-6-Trichlorophenol	88-06-2
Nitrobenzene-d5(Surr.)		2-Chloronaphthalene	91-58-7
2-Fluorobiphenyl(Surr.)	321-60-8	1-Chloronaphthalene	90-13-1
2-4-6-Tribromophenol(Surr.)		2-Nitroaniline	88-74-4
Terphenyl-d14(Surr.)	1718-51-0	Dimethyl-phthalate	131-11-3
2-Picoline	109-06-8	2-6-Dinitrotoluene	121-14-2
Phenol	108-95-2	Acenaphthylene	208-96-8
Aniline	62-53-3	3-Nitroaniline	99-09-2
Bis(2-chloroethyl)-Ether	111-44-4	Acenaphthene	83-32-9
2-Chlorophenol	95-57-8	2-4-Dinitrophenol	51-28-5
1-3-Dichlorobenzene	541-73-1	Pentachlorobenzene	608-93-5
1-4-Dichlorobenzene	106-46-7	4-Nitrophenol	100-02-7
Benzyl-alcohol	100-51-6	Dibenzofuran	132-64-9
1-2-Dichlorobenzene	95-50-1	2-4-Dinitrotoluene	121-14-2
2-Methylphenol	95-48-7	2-Naphthylamine	91-59-8
N-Nitroso-di-n-propylamine	621-64-7	2-3-4-6-Tertrachlorophenol	58-90-2
Acetophenone	98-86-2	1-Naphthylamine	134-32-7
4-Methylphenol	95-48-7	Diethyl-phthalate	84-66-2
Hexachloroethane	67-72-1	Fluorene	86-73-7
Nitrobenzene	98-95-3	4-Chlorophenyl-phenyl-ether	7005-72-3
N-Nitrosopiperidine	100-75-4	4-Nitroaniline	100-01-6
Isophorone	78-59-1	4-6-Dinitro-2-methylphenol	534-52-1
2-Nitrophenol	88-75-5	Diphenylamine	122-39-4
2-4-Dimethylphenol	105-67-9	1-2-Diphenylhydrazine	122-66-7
Benzoic-acid	65-85-0	Phenacetin	62-44-2
Bis(2-chloroethoxy)methane	111-91-1	4-Bromophenyl-phenyl-ether	101-55-3
2-4-Dichlorophenol	120-83-2	Hexachlorobenzene	118-74-1
1-2-4-Trichlorobenzene	120-82-1	Pentachlorophenol	87-86-5
Naphthalene	91-20-3	Pentachloronitrobenzene	82-68-8
2-6-Dichlorophenol	87-65-0	4-Aminobiphenyl	92-67-1
4-Chloroaniline	106-47-8	Pronamide	23950-58-5
Dimethylaminoazobenzene	60-11-7	Phenanthrene	85-01-8
Butyl-benzyl-phthalate	85-68-7	Anthracene	120-12-7
3-3'-Dichlorobenzidene	91-94-1	Di-n-butyl-phthalate	84-74-2
Benzo[a]anthracene	56-55-3	Fluoranthene	206-44-0
Chrysene	218-01-9	Pyrene	129-00-0

Table 4: Analytical Methods for Semivolatile Organic Compounds

Compound	CAS Number	Compound	CAS Number
Bis(2-ethylhexyl)phthalate	117-81-7	Dibenzo[a-j)acridine	224-42-0
Di-n-octyl-phthalate	117-84-0	Indeno[1-2-3-cd]pyrene	193-39-5
Benzo(b)fluoranthene	205-99-2	Dibenz[a-h]anthracene	53-70-3
Dimethylbenz(a)anthracene	57-97-6	Benzo[g-h-i]perylene	191-24-2
Benzo(k)fluoranthene	207-08-9	Methylmethanesulfonate	66-27-3
Benzo(a)pyrene	50-32-8	Ethylmethanesulfonate	62-50-0
3-Methylcholanthrene	56-49-5		

Pesticides Analysis

Analyze pesticide compounds by an Arkansas accredited commercial laboratory using SW-846 Method 8270D Rev. 4, 2/2007, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry," or a more recently approved revision.

Table 5: Analytical Methods for Pesticides

Compound	CAS Number	Compound	CAS Number
1,4-Dichlorobenzene-d4 (IS)	3855-82-1	Hexachlorobenzene	118-74-1
Naphthalene-d8 (IS)	1146-65-2	Delta-BHC	319-86-8
Acenaphthene-d10 (IS)	15067-26-2	Permethrin	52645-53-1
Phenanthrene-d10 (IS)	1517-22-2	Dimethazone	81777-89-1
Chrysene-d12 (IS)	1719-22-2	Methoxychlor	72-43-5
Nitrobenzene-d5(Surr.)	4165-60-0	Methyl-Parathion	298-00-0
2-Fluorobiphenyl(Surr.)	321-60-8	Alachlor	15972-60-8
Terphenyl-d14(Surr.)	1718-51-0	Aldrin	309-00-2
2-4-6-Tribromophenol(Surr.)	118-79-6	Heptachlor	76-44-8
2-Fluorophenol (Surr.)	367-12-4	Malathion	121-75-5
Trifluralin	1582-09-8	Chlorpyrifos	2921-88-2
Alpha-BHC	319-84-6	Endrin Aldehyde	7421-93-4
Simazine	122-34-9	p-p'-DDE	72-55-9
Atrazine	1912-24-9	Pendimethalin	40487-42-1
Beta-BHC	319-85-7	Heptachlor-Epoxide	1024-57-3
Propazine	139-40-2	p-p'-DDD	72-54-8
Gamma-BHC	58-89-9	Endosulfan-I	959-98-8
Diazinon	333-41-5	Endosulfan-Sulfate	1031-07-8
Dieldrin	60-57-1	p-p'-DDT	50-29-3
Endrin	72-20-8	Endrin Ketone	53494-70-5
Endosulfan-II	33213-65-9		

Decontamination and Waste Disposal

Do not generate decontamination waste. Collect and recycle by a hazardous waste treatment facility all waste solvents generated by extraction procedures.

Specific Performance Requirements

There are no specific performance requirements for the elements of this project.

Corrective Actions

The analyst must document whenever a problem exists with the sample, sample data, or QC data. Use the Corrective Action and Preventive Action (CAPA) Form to document problems and corrective actions with the sample, (holding time errors, preservation errors) sample data, (outliers, matrix interference) or QC data (out of control). The QA Officer and/or Lab Supervisor will review the CAPA. The QA Officer and/or Lab Supervisor must sign off on any data that must be voided or qualified.

Laboratory personnel will document problems with sample conditions upon receipt by the lab on the COC form and contact the sampler. Corrective actions include training and communication of sampling requirements.

Table 6: Quality Control Activity, Acceptance Criteria, and Corrective Action

QC Activity	Acceptance Criteria	Corrective Action
Initial Instrument Blank	Response < LOQ	Prepare another blank, determine cause
Initial Calibration	Coefficient of Variation > 0.995	Reanalyze standards, make new standards
QC Check Standard	Method or lab established limits	Reanalyze, prepare new QC check standard
Continuing Calibration	Method Limits	Recalibrate and reanalyze samples
Sample Duplicates	Precision within Limits	Reanalyze, qualify results
Matrix Spike Duplicates	Recoveries and Precision within Limits	Reanalyze, determine cause, qualify results
Analytical Balance Calibration	Series of NIST traceable weights Must weigh within established limits	Recalibrate and re-weigh NIST traceable weights
Refrigerator Temperature	$\leq 6°C$	Adjust refrigerator Temperature

Element B5: Quality Control Requirements

Sampling

Collect field duplicate samples and in-situ measurements at a rate of 10% or a minimum of one per week if less than ten samples are collected per week per field personnel. At the field duplicate site, collect an additional grab sample, an additional metals sample, three additional total organic carbon (TOC) samples, an additional pesticide sample, and all field measurements if they were originally collected.

Laboratory

Assure data quality from the laboratory using a system of internal checks. These include equipment checks, reagent checks, and laboratory performance checks. Record results to verify the quality control system and to monitor any changes that occur.

Chemical Laboratory

- Each day before use, check all analytical balances for calibration using a series of National Institute for Standards and Technology (NIST) traceable weights demonstrating the range of the balance (1g, 20g, 50g, and 100g). The balance reading for each weight should be within a range of acceptability for the balance to meet calibration check requirements. Calibrate balance if any reading falls outside of the range of acceptability. Calculate the range of acceptability annually for each balance by calculating the average and standard deviation of a minimum of the last twenty readings of each weight. The acceptability limits are then defined as the average ±3 standard deviations.
- A datalogger automatically records the temperature of biological oxygen demand (BOD) incubator twice daily at twelve-hour. The temperature is 20 +/- 1.0 °C at all times. Take corrective action, adjustment or repair, if this temperature range is not met.
- Record the temperature of all residue drying ovens at the beginning and end of the drying cycle on the total suspended solids/total dissolved solids (TSS/TDS) Temperature Log sheet. The temperature criteria are 103-105 °C for TSS filters and the evaporation portion of the TDS process; and 180 ±2°C for the final drying stage of TDS samples. Take corrective action, adjustment, or repair if these temperatures are not correct.
- Record the results of each pH calibration in the pH calibration log book. Take corrective action if the electrode response to two buffers shows differences greater than 0.1 pH unit. If recalibration, cleaning the electrodes, or changing the buffers does not solve the issue replace the electrodes.

Laboratory Performance Checks

Check the performance of the laboratory using duplicate matrix spiked samples, laboratory control spiked samples, matrix spike/matrix spike duplicate pairs if appropriate for the analysis, and check samples from an outside source. See bullets below for type and frequency of each.

- Check all chemical analyses possible for accuracy by the analysis of LCS. Analyze a minimum of one LCS per batch of twenty samples. Prepare spike samples by the addition of a known amount of target analyte(s) to an aliquot of de-ionized water, free of target analytes and organics. Compare LCS recoveries to method or lab generated acceptance criteria. Enter results in the LIMS QC system and verified to be within the control limits.

- Laboratory precision and the effects of the matrix on analyte recovery is determined by the preparation and analysis of a minimum of one Matrix Spike/Matrix Spike Duplicate (MS/MSD) per batch of twenty samples. MS/MSD are prepared by adding a known amount of target analyte(s) to an aliquot of the sample which has a field duplicate. Compare the precision and recoveries of the MS/MSD to method or lab generated acceptance criteria. Enter he results in the LIMS and verified to be within the control limits
- Analyze check samples from an outside source semi-annually. Purchase Proficiency Testing (PT) samples from a The NELAC Institute (TNI) approved vendor. The expected values of the PT samples are unknown to the analyst at the time of analysis.
- For bacteriological samples, perform a positive control (a known reference standard) and sterility checks as per the method. These controls demonstrate the efficiency of the analytical process and the absence of contaminants or interferences. Analyze two sterility checks per analytical batch of samples, filter one before any samples and one after all samples are filtered. For fecal analysis, perform monthly verifications of blue colonies as required by the Clean Water Act Methods Update Rule for the Analysis of Effluent, 40 CFR Part 136, Federal Register Vol. 82, No. 165, Monday, August 27, 2017.

Procedures to Assess Data Precision and Accuracy

Assess precision and accuracy of all laboratory data immediately after analyses are performed. Enter data from all duplicate and spiked samples into LIMS which will check them against the acceptance criteria, and qualify violations.

Precision

- Determine data precision from field duplicate samples and laboratory spiked replicate samples.
- Determine control limits for precision by either method specified or historical data. Discard outlier data before calculations are made. Determine a series of control limits for different concentration ranges when necessary.

Field Precision

- Base field precision on the relative percent difference between the sample and its field duplicate. Base control limits on laboratory established limits. Calculate the RPD as follows:

$$RPD = (\{Duplicate - Original\}/\{(Duplicate + Original)/2\})*100$$

Laboratory Precision

- Evaluate laboratory precision from laboratory spiked replicate samples. Base control limits on method control limits or lab established limits.
- Calculate RPD as follows:

$$RPD = \{Duplicate - Original\}/\{\{Duplicate + Original\}/2\}*100$$

Accuracy

- Base control limits for accuracy on method or lab established limits and upon the percent recovery of the Laboratory Control Samples (LCS).
- The percent recovery, P, is defined as:

$$P = \{(Final\ Concentration - Initial\ Concentration)/Spike\ added\}\ X100$$

- Consider the analysis out of control when the percent recovery of the LCS is outside the acceptance criteria for that parameter.

Corrective Action

- The purpose of a corrective action is to document and promptly address major and/or minor problems, and to develop a plan that will eliminate the potential for repetition of the problem.
- Corrective actions are taken when:
  - Quality control checks reveal a problem.
  - The QC data are out of control.
  - Deficiencies are cited during an audit.
  - Samples are lost.

Table 7: Acceptance Criteria and Corrective Actions for Quality Control Checks

QC check	Acceptance Criteria	Corrective Actions
Reagent blanks	< Reporting limit	Verify reagent sources. Review preparation and storage procedures. Discard contaminated reagent. Document on incident report.
Field blanks	< Reporting limit	Re-prep, re-analyze if allowed by holding time; If analytes are still present in the field blank, properly qualify positive analytes in the field blank and samples; address in the case narrative of the final report.
LCS	% recovery within method specified OR laboratory established limits	Check spiking solution; re-prep LCS and re-analyze LCS with associated samples.
Sample loss		Occasionally a sample is lost (spilled, unpreserved, misplaced) either in the field or the laboratory. If this occurs while sampling, a replacement sample can be collected immediately. If the loss occurs later in the day, a replacement sample may be collected, but the sample should be treated as a separate sample, additional in-situ data should be taken and the sample recorded on a separate line of the COC. If it is not possible to collect a new sample, or the sample is lost in the laboratory, no additional sampling should occur.

Table 8: Duplicates and Matrix Spikes

Duplicate Type	Corrective Action
Field Duplicates	Reanalyze samples. Examine samples for visual difference if samples are still out of control, qualify RPD results. Document on CAPA.
Matrix Spikes/Matrix Spike Duplicates	Reanalyze samples. Check spike solution. Check for matrix interferences. Document on CAPA. Qualify affected samples.

Acceptance Criteria and Corrective Actions for Performance Evaluation (PE) Samples

The sample provider will determine acceptance criteria for PE samples. All results marked "not acceptable" will require corrective actions and written explanations to the QA Officer. Corrective actions will be to:

- Check calculations and data transcription.
- Check calibration and calibration standards.
- Investigate possibility of analyst error or improper technique.
- Investigate possibility of instrument malfunction.
- Investigate possibility of matrix interference.
- Document corrective actions.

The analyst must document whenever a problem exists with samples, sample data, or QC data. Use the CAPA Form to document problems with samples, (holding time errors, preservation errors) sample data, (outliers, matrix interference) or QC data (out of control). The QA Officer and/or Lab Supervisor will review the CAPA form. The QA Officer or Lab Supervisor must sign off on any data that must be voided or qualified.

Representativeness

Determining whether the results from a sample represent the true values in the stream being sampled is controlled by the sampling process. The Project Manager is responsible for site selection. The Field Coordinator is responsible for sampling procedures and sampler training. Assess actual representativeness from the field duplicates. The control limits set for each field duplicate parameter are meant to assure proper sampling techniques.

Comparability

- Analytical methodology.
  - EPA approved methods and/or current methods from *Standard Methods for the Examination of Water and Wastewater,* will be used. All water data generated will be entered into the WQX with the appropriate parameter code and with the standard units.
- Performance Evaluation Samples.
  - The laboratory will participate in two performance evaluation studies annually from a TNI approved performance evaluation provider. These studies document the laboratory's ability and compare our results with other laboratories throughout the country.

Completeness

The work plan for monitoring lists the CSI sites to be conducted during the federal fiscal year. A mid-year and an end-of-year progress report, incorporating the number of ambient samples and CSI samples collected is prepared for the Project Manager.

Element B6: Instrument Maintenance Requirements

Inspections and Acceptance Testing of Instruments

All instruments should meet specific performance criteria before acceptance. The use of environmental matrix spike QC samples will be used for these tests.

Each instrument will be inspected during its scheduled cleaning as per manufacturers' recommendations or operating instructions.

Final Acceptance

The LCS will perform the final acceptance to assure compliance with requirements.

Resolution of Deficiencies

If deficiencies are found during the testing procedure the vendor will be given every opportunity to correct the problem within the available time allowed by the project and funding mechanisms.

Preventive Maintenance

Follow manufactures' recommendations for preventive. Calibration checks, and probe and power source condition checks are examples of activities that could occur during preventive maintenance activities.
ADEE Laboratory Services follows preventive maintenance and calibration protocols provided by the manufacturer's instructions and/or laboratory SOPs.

- Analytical Balance: SOP #QA-401, "Routine Balance Check and Calibration," most recent revision.
- Dissolved Oxygen Meters: SOP # WC-101, "Determination of Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand in Surface Waters," most recent revision.
- pH Meter: probe/meter user manuals and SOP # WC-107, "Determination of pH in Surface Waters, Soils, and Wastes," most recent revision.
- Specific Conductance Meter: instrument user manual and SOP # WC-112, "The Determination of Specific Conductance," most recent revision.
- Nutrient analyses: autoanalyzer's manufacturer's manual and SOP #WC-103, "The Determination of Ammonia, Orthophosphate, and Nitrate+Nitrite in Surface water, Wastewater, and Groundwater via Flow Injection Analysis," most recent revision. Also, SOP #WC-105, "The Determination of Total Kjeldahl Nitrogen (TKN) and Total Phosphorus in Surface water, Wastewater, and Groundwater via Flow Injection Analysis," most recent revision.
- Anions analyses: manufacturer's user manual, and SOP #WC-109, "The Determination of Anions in Surface Waters, Wastewater, and Solids via Ion Chromatography," most recent revision.
- Total Organic Carbon (TOC) analysis: instrument manuals and SOP#WC-110, "The Determination of Total Organic Carbon in Surface Waters and Soils via UV/Persulfate Oxidation Method," most recent revision.

- Volatile organic compounds (VOCs): Gas chromatograph/mass spectrometer instrument manuals and SOP #C-300, "Volatile Organic Compounds by GC/MS in Water and Soils," most recent revision.
- Semivolatile organic compounds (SVOCs): Gas chromatograph/mass spectrometer instrument manuals and SOP #C-301, "Semi-Volatile Organic Compounds by GC/MS Water and Soils," most recent revision.
- ICP/OES System used for total and dissolved metals analysis: instrument manual and SOP #M-203, "Sample Analysis by Inductively Coupled Plasma—Optical Emission Spectrometry (ICP-PES) by 200.7/6010D," most recent revision.
- ICP/MS System used for total and dissolved metals analysis: instrument manual and SOP #M-200, "Sample Analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) by 200.8 or 200.8/6020B," most recent revision.
- Turbidity: instrument manual and SOP #WC-108, "The Determination of Turbidity by Nephelometry (EPA 180.1)," most recent revision.
- Chlorophyll A, Optical Brighteners, and Phycocyanin analyses: fluorometer user manual and the most recent revisions of SOP #WC-104, "The Determination of Chlorophyll A (EPA 445.0 Modified)," SOP #WC-117, "The Determination of Optical Brightener Agents (OBAs)," or SOP #WC-121, "The Determination of Phycocyanin (EPA 445.0 Modified).
- Fecal and E. coli analyses: IDEXX user instructions, and the most recent revisions of SOP #WC-122 "Detection of Fecal Coliforms in Water; IDEXX Colilert-18 Test Method," and SOP #WC-123 "Detection of E. coli in Water; IDEXX Colilert-18 Test Method.".
- Deionizer Water Unit: the quality of water used in the ADEE Laboratory is monitored weekly by the analysis of method blanks for conductivity, anions, nutrients, TOC, and metals. Any anomaly in method blank results such as positive results, is addressed by corrective action measures such as changing out the ion-exchange cartridges and filters.

Element B7: Calibrating Procedures

Calibration, the process of adjusting a piece of equipment to ensure it gives accurate answers, is one of the most important steps in any analysis. All equipment must be routinely calibrated. Calibrate field instruments prior to use and maintain individual calibration logs. Calibrate multi-parameter sondes before and after multi-day deployments. DEQ standard operating procedural manuals describe calibration requirements for field and laboratory instruments. Do not use data that do not meet calibration and post calibration specifications for Clean Water Act purposes.

Stock Standard Receipt and Traceability

- Purchased Standards
  - Purchase stock standards from reputable vendors. They should be NIST traceable, and labeled with a lot number and an expiration number. Retain electronic copies of Certificates of Analysis in the LIMS system for future reference. Document stock standards in the LIMS system and assign a unique inventory identification number.
- Prepared Standards
  - Document standards prepared from pure compounds in the LIMS system and assign a unique inventory identification number. This information includes: manufacturer; lot number; expiration date; weights and volumes taken; final concentration; and preparer's initials
- Intermediate Standards and Spiking Solutions
  - Record the preparation of intermediate dilutions, mixed standards and spiking solutions in the LIMS system and assign a unique inventory identification number.
  - Information recorded must include: lot number of the stock; concentration of the stock used; volume of the stock taken; final volume; final concentration of each component; preparers initials; date.
- Calibration Standards
  - Prepare calibration standards from stock or intermediate standards.
  - Document preparation of the standards in the LIMS system.
  - The information recorded must include: lot number of the stock; concentration of the stock used; volume of the stock taken; final volume; final concentration of each component; preparers initials; date.
- Instrument Calibration
  - All calibrations for laboratory analysis follow method guidelines and are specifically detailed in the SOPs listed in Element B6, Instrument Maintenance Requirements.

Element B8: Inspection/Acceptance Requirements for Supplies and Consumables

The laboratory supervisor or the project coordinator will purchase supplies and consumables. The DEQ mail room or laboratory personnel will receive ordered items. The individual receiving the items will inspect the material and check it against the packing slip.

Date all chemicals and reagents and inspect for proper expiration date. Purchase chemical standards used for calibration in the laboratory from reputable vendors with Certificates of Analysis listing the certified chemical content. Calibration materials such as thermometers and weights are traceable to NIST or American Society of the International Association for Testing and Materials (ASTM).

Element B9: Data Acquisition Requirements (Non-Direct Measures)

No data will be collected or used from non-measurement sources.

Element B10: Data Management

Field Data

Record data collected in the field in both the field book and on the COC. Upon receipt of the sample by the lab, enter the sample data, date of receipt, time, and station number into LIMS and issue a laboratory log number. Enter in-situ data (such as in stream water temperature, dissolved oxygen, pH, and flow severity) into LIMS after it has been checked for reasonable results by the data entry analyst. Verify abnormally high or low temperatures, pH, or dissolved oxygen results are verified with the sampler.

Laboratory Data

- Manual Methods:
  - Manually enter data generated by manual procedures (chemical oxygen demand (COD), Cyanide, oil and grease (O&G)) into LIMS from lab bench sheets. The bench sheets for COD and Cyanide are located in bound lab notebooks. Oil and grease bench sheets are electronic. Lab notebooks are clearly labeled as to contents and stored for a minimum of seven years.
- Automated Methods:
  - Data generated by automated procedures, Auto Analyzer, Atomic Absorption, ICP, GCMS, etc. are directly transferred to LIMS. Data are usually processed after collection in a spreadsheet or edited to a usable form before transfer.
  - All instrument generated data are stored electronically and kept in accordance to DEQ's records retention policy.

Control Mechanisms for Detection/Correcting Errors

Data must pass all precision and accuracy checks for both the field duplicates and the laboratory matrix spike replicates. The data must be within the allowed range, *i.e.* pH between 0 and 14. Manually check data for logical errors, *i.e.* dissolved fraction greater than the total. Flag test results for dissolved copper and/or zinc if the results exceed the total recoverable results as set forth in the metals SOP.

The analyst inspects data before uploading the results into LIMS, and checks for QC failures leading to re-analysis of samples or sample dilutions. Once data are uploaded into LIMS, the system color-codes any QC failures such as positive blanks and recovers any QC samples which fall outside of acceptability limits. Data undergoes "Peer Review" which includes review of traceability, quality control, and comparison of uploaded results with "raw data."

Date are transitioned to "validated" in the LIMS system and goes to the lab manager for further review after peer review has been completed. The lab manager transitions data to "approved" in LIMS before it is released in a final report. If QC errors are noted, an investigation to determine the possible cause of the error is initiated immediately. Inspect all lab data for that 'run' to see if there are any trends or problems with multiple samples. If the error does not seem to have originated in the lab, contact the person who collected the sample concerning the findings to determine if the error may have originated in the field. When the nature and extent of the error has been determined a decision will be made as to how much data was affected and whether to flag or discard data.

Data Handling Equipment and Procedures

Acquire computer hardware and software according to the DEQ Agency Information Technology (IT) Budget and Expenditure Plan. IT is responsible for the computer and network infrastructure as well as all DEQ software needs. The datacenter is equipped with a large Uninterruptible Power Supply and generator backup that support both IT and Laboratory Services infrastructure. An off-site disaster recovery site helps maintain a backup and image of data housed at the main campus.

Programs used to process, compile and analyze the data include the WQX, and programs developed by DEQ personnel or purchased programs such as Microsoft Office.

Data Storage

Data in LIMS are stored on each computer's hard drive in the laboratory, transferred to the DEQ main computer, and backed up daily. Data from all water quality monitoring networks are regularly transferred to the WQX.

Data Use

Data generated are available to users from several sources. The Department computer system is available to staff directly and through telephone modem connections. Data in the WQX system is available to all users.

Element C1: Assessment and Response Actions

The QAO or designee will conduct an annual laboratory inspection to review and assess analytical procedures, laboratory personnel, facilities, instrumentation, laboratory quality control, and data handling. Field duties are evaluated by supervisors to assess sampling methodologies, data handling, field quality control procedures and personnel. Annual "refresher training" courses should be made available to sample collectors on sampling methodologies and quality control procedures.

The laboratory will participate in two PT studies annually purchased from a TNI approved PT provider. These studies document the laboratory's proficiency and help compare our results with other laboratories throughout the country.

In the laboratory, corrective actions are taken when:

- QC checks reveal a problem.
- The QC data are out of control.
- Deficiencies are cited during an audit.
- Data are determined to be questionable by an outlier test.

If for any of the above reasons precision and/or accuracy data fall outside control boundaries or acceptable recovery or bias standards, the analyst will consult his/her supervisor. If it is determined that the analytical system is out of control, the quality control officer is consulted and the system is brought back into control. At this time, all data sets containing precision or accuracy points that have shown the analysis to be out of control will be either re-analyzed if the holding time has not been exceeded or qualified.

Element C2: Reports to Management

An annual summary QA report may be prepared and submitted to either the QAO and/or DEQ management by the QAC, FSC, LCS, or the SSPC, if requested. The report should identify any quality assurance issue that resulted in a significant amount of data loss and the corrective measures that were immediately taken, if any, to address the issue. The report may also discuss recommendations to help prevent future QA failures and/or any actions that did occur that may help limit future QA issues. All quality assurance issues, either major (significant loss of data) or minor (meter failure) should be verbally reported to one of the above individuals as soon as possible. Minor QA issues may or may not be included in the annual report.

The LSC, or a designee, may prepare a report that includes metrics of samples analyzed, percent of qualified data, systems audits and other QA metrics, if requested. The report may also discuss recommendations to help prevent future QA failures and/or any actions that did occur that may help limit future QA issues.

A semi-annual progress report may be prepared by the QAC, FSC, or SSPC and submitted to management, if requested. The report should discuss the status of task completion and the work to be scheduled the next half of the year.

One additional report that may be prepared, if requested, is the results of a periodic evaluation the data produced by the projects associated with this QAPP. The report may include information such an assessment of the data quality in terms of precision, accuracy and completeness of the project as described in Element D1, 2 and 3.

As a result of these reports, senior management may or may not instruct senior staff members to establish training or educational opportunities to enhance the quality assurance knowledge of field staff. These opportunities may include training on new sampling and preservation methods, documentation records, corrective action procedures, and other QA related activity.

Element D1: Data Review, Validation, and Verification Requirements

Data integrity must be validated prior to entry into the database. The Chemist Supervisor is responsible for ensuring laboratory data are properly reviewed and verified, and are in the proper format for submittal to storage databases. The FSC and SSPC are responsible for ensuring all field and biological data are properly reviewed and verified and are in the proper format for submittal to storage databases. All data produced must meet data quality objectives outlined in Element A7. Data that do not meet data quality objectives as outlined in Element A7 will not be input into data storage data bases.

Element D2: Validation and Verification Methods

Data Verification

Verification refers to the process of confirming a process or procedure was followed. Data verification is performed using self-assessments and by a technical review by the laboratory and project managers. Data to be verified are evaluated against project specifications and are checked for errors in transcriptions, calculations, and data input. Potential outliers are handled by the procedure listed below. Issues that can be resolved will be corrected and documented. The laboratory or project manager will consult with higher level managers if irresolvable issues occur to establish an appropriate course of action.

Data Validation

The FSC, SSPC and the LCS are responsible for validating that the verified data are usable and reportable. They are also responsible for reevaluating the data to determine whether any anomalies are present.

Data integrity will be verified at several points during the collection and reporting process. The two principal check points are laboratory quality control checks and data processing checks made during the data preparation for entry into WQX.

The laboratory control checks are described in Element B5. These checks consist of use of field duplicates, laboratory duplicates, and spikes to monitor the levels of precision and accuracy of the collection and analytical processes.

The data processing checks are designed to assure the accurate transfer of the data from the laboratory report forms to the computer system. The data are verified by a computer program which inspects the data for values out of the permissible or normal range.

Outliers

- Quality Control Data
  - Outliers from the laboratory quality control checks indicate sampling or analytical problems. Re-analyze all samples in these out-of-control situations. If re-analysis is impossible examine data for obvious causes.
  - If reasons are found for the problem, e.g. dilution error or field duplicate samples are obviously different, the QC data will not be used in the database to calculate new control limits. If the analytical process is found to be on control, based on other control samples in the same analysis set, the data for the samples can be used.
  - If reasons for the problem are not found, test the QC data to see if it is an outlier. If the test results do not justify calling the suspect data point an outlier use the data in the QC database to calculate new control limits.
- Sample Data
  - When a value in a data set is suspiciously high or low, examine to see if it must be discarded to avoid biasing the data set. The first check should be to see if there is any physical reason, e.g. high flow, low flow, abnormal temperature, or any other explanation for the abnormal data.
  - If a reason for the "odd" value is not found it must be tested to see if it is statistically judged to be an outlier. The suspect data point and the eleven closest data points in the data set should be used in the test.

Element D3: Reconciliation with Data Quality Objectives

Results obtained from projects associated with this QAPP are evaluated periodically and at the end of the project to determine if data quality objectives are being, or have been, obtained. Project completeness will be reconciled with the expected outputs. Data precision and accuracy developed for the project will be reported to the decision makers to establish the limits that should be placed on the data.

Data generated by projects associated with this QAPP that meet the QA/QC requirements set forth by this QAPP may be used to establish trend analyses, background or baseline levels of water quality criteria, and indicate those areas of the State which may need more intensive monitoring. Data produced from this project may be used to determine attainment of water quality criteria.

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