ARKANSAS' WATER QUALITY

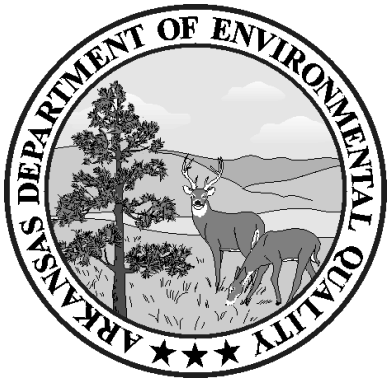
AND

COMPLIANCE MONITORING

QUALITY ASSURANCE PROJECT PLAN

(QTRAK #16-155)

ARKANSAS DEPARTMENT OF ENVIRONMENTAL QUALITY



5301 Northshore Drive
North Little Rock, Arkansas 72118

February 2016

QUALITY ASSURANCE PROJECT PLAN
FOR
ARKANSAS'S WATER QUALITY AND COMPLIANCE MONITORING
QTRAK# ???-???

APPROVAL:

USEPA Approving Official _____ Date 3/2/2016
Mr. Curry Jones, Chief
State/Tribal Programs Section, Region 6

U.S. EPA Project Officer _____ Date 3/2/2016
Ms. Arlene Gaines

ADEQ QAPP Officer Penny Semberski Date 12/14/15
Ms. Penny Semberski

ADEQ Project Manager _____ Date 12-22-15
Ms. Sarah Clem

ADEQ Chemist Supervisor _____ Date 12/14/15
Mr. Jeff Ruehr

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ELEMENT A2: TABLE OF CONTENTS

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ELEMENT A3: DISTRIBUTION LIST

The following individuals will receive a copy of, or have access to this QAPP:

U.S. Environmental Protection Agency

Ms. Arlene Gaines
Project Officer
State/Tribal Programs Section (6WQ-AT)

Arkansas Department of Environmental Quality

Ms. Penny Semberski
State Q.A. Officer

Water Division

Ms. Sarah Clem
Project Manager

Jason Bolenbaugh
Field Coordinator

Environmental Preservation/Technical Services Division

Mr. Jeff Ruehr
ADEQ Chemist Supervisor

ELEMENT A4: PROJECT/TASK ORGANIZATION

Personnel from the Water Division and are responsible for collecting the water quality samples, the Compliance Sampling Inspection (CSI) samples, macroinvertebrate and fish community samples, sediment samples, and the samples collected for toxicity testing. All chemical analyses and quality assurance of the chemical analyses will be completed by the Technical Services Division. Biological analysis, and its associated quality assurance, and data processing and assessment will be performed by personnel in both the Water Division and Technical Services Division.

PROJECT MANAGER:
Ms. Sarah Clem, Water Division Planning Branch Manager will be the Project Manager for Ambient Water Quality Monitoring and Compliance Sampling Project. In the absence of Ms. Sarah Clem, Mr. Jim Wise will assume responsibilities. Responsibilities include:

Overall project management
Assignment of Water Division personnel to the project
Ensuring all procedures and reports meet QA requirements
Approval of sampling/work plans and analytical parameters

FIELD COORDINATOR (Ambient Water Samples & Compliance Sampling Inspections):
The Field Coordinator for the project is Mr. Jason Bolenbaugh. Responsibilities include:

Ensuring that all field equipment and instruments meet performance and calibration criteria
Ensuring that proper labeling, handling, storage, and shipping requirements have been met
Assignment of Field Services personnel to the project
Scheduling of field activities as they relate to Field Services personnel
Selection and scheduling of all compliance sampling inspections
Approving all compliance sampling reports

QA OFFICER:
The QA officer for the project is Ms. Penny Semberski, Chemist Supervisor. Responsibilities include management and implementation of the Quality Assurance Program and the Laboratory Certification Program. Specific duties for this project include:

Certification of Laboratories

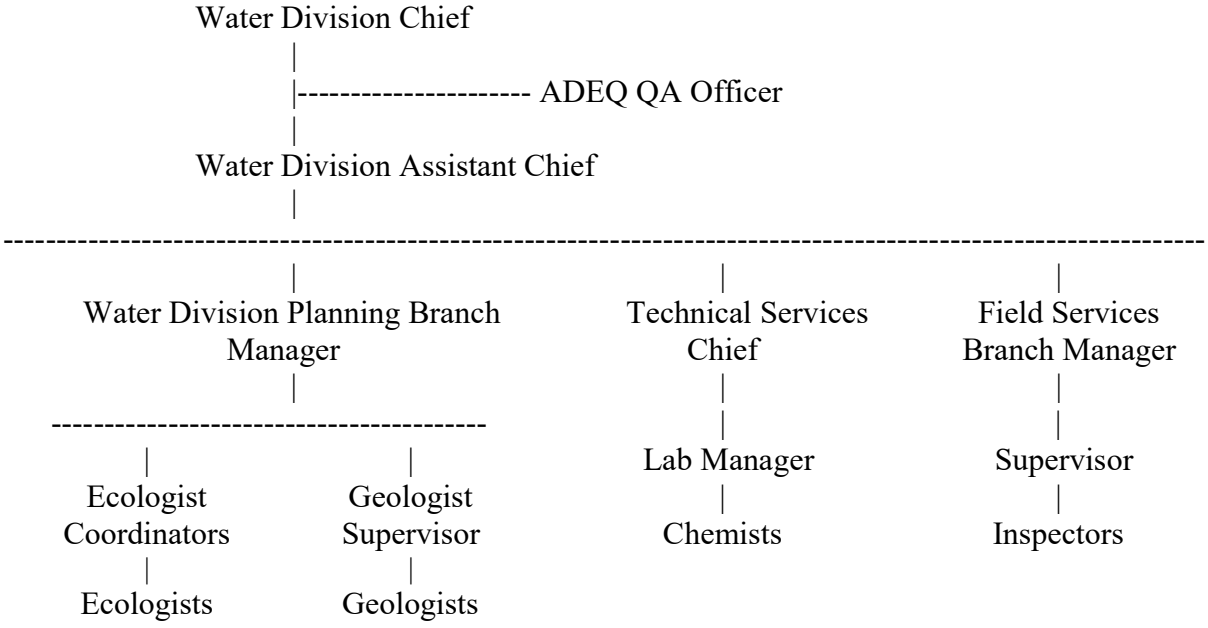
Annual field audits of field sampling activities with field personnel will be conducted by the QA Officer or designated personnel
Annual audits of laboratory analysis procedures, equipment maintenance, and performance
Annual review of the QAPP for accuracy to the project

LABORATORY COORDINATOR:
The laboratory coordinator for this project is Mr. Jeff Ruehr. Responsibilities include:

The official organizational contact for all QA matters for the project
Ensuring that all required QA activities are performed including performance evaluations
All laboratory functions related to this project
Ensuring that all laboratory functions meet QA requirements
Receiving all consumables and perishables laboratory supplies
Laboratory data management.

The Organizational Charts (Appendix 1) includes the personnel involved in the program. The Project Organization chart outlines the lines of authority.

Project Organizational Chart



ELEMENT A5: PROBLEM DEFINITION/BACKGROUND

Surface Water Monitoring History

The ambient river and stream monitoring program, which began in 1974, was 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 physical, chemical, and biological data, as well as seasonal and other variations. The monitoring program helped to establish cause and effect relationships between known point and nonpoint sources of pollution and the quality of the State's waters. The ambient monitoring network will always be vital in evaluating the effectiveness of ADEQ's pollution control program by assessing overall water quality before and after the implementation of pollution controls.

During 1982, the Department reevaluated the monitoring network and four goals were established for the new network:

1) To better assess the effects of point source dischargers upon water quality;
2) To observe the impact of known nonpoint source problems over the long term;
3) To continue monitoring Arkansas' major rivers; and
4) 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.

Problem Statement

Some of the basic objectives of the water quality monitoring networks are to provide background water quality data as well as 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, as well as determination of pollution control efforts, reliable assessment methodologies, and the development of defensible water quality regulations. This data may be used by the Water Quality Management Planning Branch, Water Division, 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 meeting designated uses.

Water Quality Monitoring Networks

The Department operates an integrated water quality monitoring program that consists of: 1) Routine Water Quality Monitoring Activities for surface and ground waters; 2) Non-Routine Water Quality Monitoring Activities for surface and ground waters; 3) Compliance Sampling Inspections; and 4) Education and Outreach Programs. The "State of Arkansas Water Quality Monitoring and Assessment Program, Revision 5, January 2013" describes the monitoring activities of the Department as well as the goals, data management procedures, support and infrastructure, and quality assurance requirements of the program.

Arkansas's water quality standards for lakes have been adapted from the surface water quality standards for streams. The designated use support or non-support assessment is based on a certain percentage of the data points exceeding the criteria set to protect the use. Because the current assessment method and water quality criteria were established using data from Arkansas♠s Ambient Water Quality Monitoring Network as discussed in the latest version of "The State Of Arkansas Water Quality Monitoring and Assessment Program," Revision 5, January 2013. that monitors Arkansas♠ rivers and streams on a monthly basis, it is not well adapted to assess lake-water quality where only a few data points exist. Although the designated uses that are assigned to Arkansas's lakes may be appropriate, the criteria set forth to protect them individually may require additional considerations. Arkansas's lakes are highly variable in water quality, morphology, watershed characteristics, purposes, operation and management activities, and naturally occurring influences.

Setting specific lake standards for Arkansas's lakes presents many problems. Adopting criteria to protect a specific designated use may interfere with other designated uses for the same waterbody. For example, Chlorophyll a, phosphorus, or water clarity criteria may be designed to protect the drinking water use or certain recreational uses of a lake, but they may be counter-productive for lakes created for the primary purpose of public fishing.

ELEMENT A6: PROJECT TASK DESCRIPTION

The surface and ground water ambient monitoring programs are designed to evaluate and establish water quality trends in the State's waters. The program's objectives are discussed in the "The State Of Arkansas Water Quality Monitoring and Assessment Program," Revision 5, January 2013.

The current CWA Sections 106 and 604(b) work plans submitted to EPA Region 6 outlines the tasks to be performed and the schedule of when the work is projected to be completed.

The **Ambient Water Quality Monitoring Network** consists of stations sampled monthly and analyzed for the parameters listed in the current CWA Sections 106 and 604(b) work plan. The sample stations and their locations are also listed in the work plan. Flow measurements are provided by the U.S. Geological Service at those stations indicated in the work plan. Flows are either taken by continuous read gages, or wire or staff gages read monthly by USGS or ADEQ personnel.

The **Roving Water Quality Monitoring Network** sample sites are located throughout the state. Usually, between 30 and 40 sites are collected from one section of the state for two years on a bi-monthly basis. The samples are analyzed for the same parameters as the ambient water quality monitoring stations. In addition, non-routine constituents, such as *E. coli* bacteria and pesticides, may be collected.

The **Ground Water Quality Monitoring Network** presently contains 11 monitoring areas with a total of 280 springs and wells. The monitoring locations are found in several reports; although the status report provides the best source for documenting the locations of all stations. Field parameters should be taken at all sites and include temperature, pH, conductance, dissolved oxygen, and Oxidation-Reduction Potential. Samples taken for laboratory analyses differ for each location but generally include major cations and anions, total and dissolved metals, nutrients, and total organic carbon, plus volatiles and semivolatiles - including a pesticide scan, in selected areas. The current CWA Sections 106 and 604(b) work plan outlines the schedule of work.

The NPDES **Compliance Sampling Inspections** are to verify compliance with effluent limitations and to evaluate the permittee self-monitoring program. The sampling schedule is listed in the current CWA Section 106 and 604(b) work plan.

Ground water monitoring at regulated sites is rare and only occurs in instances where data is suspect. A split-sampling episode is required for verification purposes. The EPA will be notified in a quarterly report when such instances occur.

The objective of the **lakes survey** is to collect water quality information to aid in the development of water quality standards. The criteria developed may be applied in assessments for the purpose of meeting the requirements of section 305(b) of the Clean Water Act.

The primary activity of this survey is to collect water samples from lakes to determine current water quality conditions for potential reference lake determination. The process is outlined in the most recent survey plan, "Water Quality of Potential Reference Lakes in Arkansas". Samples are collected at the locations described in the plan and may be analyzed for nitrate+nitrite nitrogen, total phosphorus, ortho-phosphorus, ammonia nitrogen, chlorides, sulfates, total dissolved solids, turbidity, total suspended solids, alkalinity, conductivity, total organic carbon, and chlorophyll a. In-situ measurements collected include dissolved oxygen, dissolved oxygen saturation, pH, and temperature profiles, as well as Secchi disk transparency. Field observations should be recorded to include climatic conditions, air temperature, lake-surface condition, unusual occurrences, and quality assurance/quality control issues.

Multi-parameter Sondes are deployed for a 72-hour period in mid to late summer at each lake site and record diurnal dissolved oxygen, pH, temperature, turbidity, and specific conductance, usually at 30-minute intervals. These monitors are positioned three feet beneath the water surface not to exceed one-half of the lake depth. Any deviations will be addressed in the work plan. Water-quality monitors are secured to fishing piers, flooded timber, or buoys. If no fishing piers or flooded timber is available, the monitors may be secured to poles or floats that will be anchored or driven into the bottom substrate.

Personnel

Department personnel will be used to perform all field duties.

Assessment Tools Needed

The Department's QA Officer or designated personnel will perform technical reviews and surveillance of field activities to establish conformity to the Department's Quality Management Plan.

The data generated will be compiled and evaluated using the most current 305(b) assessment methodology for determination of water quality standards attainment. Direct comparisons cannot always be employed, therefore best professional judgments will be utilized during data interpretation. When this occurs, an explanation as to why best professional judgement was utilized and how it was administered will accompany each occurrence.

Records Required

Field notes for field parameters measured, field equipment calibration, and any laboratory QA/QC issues will be kept at the Department for review by the Department QA Officer until project completion.

ELEMENT A7: DATA QUALITY OBJECTIVES for MEASUREMENT DATA

The objectives of the water quality monitoring programs are to provide water quality data for interpretation of: 1) designated use attainment; 2) trend analysis; 3) background or baseline water quality data establishment; and 4) water quality standards and criteria attainment. A high confidence level in the data must be attained and maintained to meet the objectives of the programs. 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.

Water Division personnel use statistical programs in Microsoft Excel and the Department's Water Quality Analysis Reporter (WQAR) program to calculate regression, standard deviations, trend analyses, percent exceedance of water quality standards, and other statistics. Trend analyses may include: 1) linear trends; 2) trends of means; 3) trends in the residuals after seasonal variations and/or serial correlation effects have been removed; and 4) significant linear trends in water quality index values for many different variables. The data are evaluated as per the most current 305(b)/303(d) assessment methodology, which is based on the most current version of the state's water quality standards, Regulation No. 2. Also, best professional judgment is used concerning outliers that pass through the QA/QC criteria. Using a long-term data set, usually five years and occasionally ten years when adequate data are available, decreases the effects of unusual climatic events such as large storm events or droughts. However, short term trend and point-in-time data analyses allow for the determination of the effects of these events. This allows for better overall water quality characterization of individual water bodies. Even though outliers may exist at any given data collection point and for any given parameter, they are generally not used in trend analyses. It is beyond the scope of these programs to characterize atypical water quality occurrences.

The support and nonsupport of designated and existing uses and the attainment of water quality standards are assessed by comparing data , as is discussed in the most current version Arkansas' "Assessment Methodology for the Preparation of the 2016 Integrated Water Quality Monitoring and Assessment Report," that is most closely associated with the use or water quality standard and the criteria protective of them. The assessment methodology is updated on a continual basis and is therefore not included in this document.

Representativeness

All measurements must be made so that the results are representative of the conditions being measured. 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 the field duplicate samples be within the acceptance criteria as outlined in Appendix 2.

Comparability

Comparability of data will be assured by using EPA approved analytical procedures and/or

current methods from *Standard Methods for the Examination of Water and Wastewater* .

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 goal for precision is to have 95% of the analyses to be within the acceptance criteria as outlined in Appendix 2. The precision requirements of the field meters are listed in Table A7-1.

Accuracy

The accuracy objectives are the control limits as determined by the procedures in Section B5, Laboratory Performance Checks section. These control limits are based upon the percent recovery of spiked samples. These control limits are listed in Appendix 2. The quantitative goal for precision is to have 95% of the laboratory matrix spikes to be within the acceptance criteria as outlined in Appendix 2. The accuracy requirements of the field meters are listed in Table A7-1.

Completeness

Completeness of data, 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 the loss of data. The quantitative goal for completeness is to have 95% of the data collected meet acceptance criteria.

TABLE A7-1: Field Meter Specifications

METER	Parameter	PRECISION	ACCURACY
YSI 556	Dissolved Oxygen	0.01 mg/L	∀ 2% reading
	Temperature	0.01EC	∀0.15EC
	Conductivity	0.001 mS/cm to 0.1 mS/cm	∀0.5% reading
	pH	0.01	∀0.20
YSI 100	pH	0.01 mg/L	∀ 0.3
	Temperature	0.10EC	∀ 0.30EC
YSI 550A	Dissolved Oxygen	0.01 mg/L	∀ 0.3
	Temperature	0.10EC	∀ 0.30EC
SonTec Flow Tracker	Instream Flow	∀ 0.003 ft/sec	∀ 1.0% of reading
Marsh-McBirney, Flowmate 2000	Instream Flow	zero stability ∀ 0.05 ft/sec	∀ 2.0% of reading
YSI Pro 1030	pH	0.01	∀0.20
	Temperature	0.10EC	∀ 0.20EC
	Conductivity	0.1 mS/cm to 1.0 mS/cm	∀1.0 % reading or 1.0 mS/cm
YSI 6920 Sonde and YSI 600XLM Sonde	Dissolved Oxygen	0.01 mg/L	∀ 2% reading
	pH	0.01	∀0.20
	Chloride	0.001 mg/L to 1 mg/L	∀15% reading
	Temperature	0.01EC	∀0.15EC
	Depth	0.001 ft, 0.001m	∀1.0 ft, ∀0.3m
	Conductivity	0.001 mS/cm to 0.1 mS/Cm	∀0.5% reading
	Turbidity	0.1 NTU	∀5.0% reading
YSI 600OMS Sonde	Dissolved Oxygen	0.01 mg/L	∀ 2% reading
	Temperature	0.01EC	∀0.15EC

METER	Parameter	PRECISION	ACCURACY
	Depth	0.001 ft, 0.001m	∀1.0 ft, ∀0.3m
	Turbidity	0.1 NTU	∀5.0% reading
	pH	0.01	∀0.20

TABLE A7-1: Field Meter Specifications

METER	Parameter	PRECISION	ACCURACY
YSI ProDSS	Dissolved Oxygen	0.01 mg/L	∀ 1% reading
	Temperature	0.1EC	∀0.2EC
	Conductivity	0.001, 0.01 or 0.1 µS/ cm (range dependent)	0 - 100 mS/cm: ±0.5% of reading or .001 mS/cm, whichever is greater 100 - 200 mS/cm: ±1.0% of reading
	pH	0.01	∀0.20
	Turbidity	0.1 NTU	0 to 999 FNU: 0.3 FNU or ±2% of reading, whichever is greater

ELEMENT A8: SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

Laboratory

Before any analyses are performed all laboratory personnel are trained and checked out on the procedures they will be responsible for performing. The person doing the training will be a senior chemist or the 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. The initial demonstration of performance studies will be kept on file for the duration of the project.

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. This training includes, but is not limited to, the following:

1. Annual training occurs as a refresher to those methods routinely used in sampling.
2. Periodic training of entire field staff when new, specialized sampling techniques for unusual constituents occur.
3. Specialized, one-on-one field training by inspector or field personnel supervisor, or QA Officer as a quality assurance function as needed, or as soon after a problem has been identified by field reports, senior staff members, or supervisors. .
4. Additional federal, state, or private sponsored training.
5. The QA Officer 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 for the duration of the project.

For sampling water quality from lakes, each team will have a leader who has had previous experience in lake water quality sampling. This will help ensure that data collected are of high quality.

ELEMENT A9: DOCUMENTATION and RECORDS

Surface and Groundwater Quality Monitoring

The raw data generated will not be displayed in a final report. The data may be used in reports after statistical calculations. The data, including raw data, bench sheets, QC checks, instruments printouts, sample chain of custody forms and field sheets may be scanned in accordance with Department policy and stored electronically for at least seven years. Water quality data will be entered into the United States Environmental Protection Agency's Water Quality Storage system if the system is available. When possible. All the data generated are available to the public by accessing either the U.S. EPA WQS data storage system.

Lake Sampling

For each site visit, the project records will include a field reporting form. Field observations recorded at the sites and on this form will include climatic conditions, air temperature, lake-surface condition, unusual occurrences, and quality assurance/quality control issues. Samples will be transported with chain-of-custody documentation. The originals of all records and documents (including soft copy versions of the data) will be maintained in accordance to ADEQ's "Records Retention Policy".

A copy of the final report will be stored electronically on ADEQ's file server.

QA Training

A report outlining the findings and recommendations of the QA Officer will be sent to the field personnel manager and the project officer. Any deficiencies noted in that report will be addressed through additional training as is outlined in Element A8

ELEMENT B1: SAMPLING PROCESS and DESIGN

General Experimental Design

The activities of this project consists of the implementation of the most recent version of "The State of Arkansas's Water Quality Monitoring and Assessment Program" (Program) and any associated work plans. This program is designed to evaluate water quality and trends in the State's waters. The 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 annual updates for the United States Environmental Protection Agency.

Types of Samples Required

The types of samples associated with this Program include water samples, bacteriological samples, metals, in situ measurements of water temperature, pH, and dissolved oxygen, and biological samples as described in Element B2.

Sampling Network Design

The Program consists of stations sampled monthly and bi-monthly as is discussed in the MAP. Water quality samples collected at these sites may be analyzed for some or all of the parameters listed in Element B4. The specific constituents to be analyzed will be determined in the associated work plan. *E. coli* bacteria may also be collected at some sites.

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

The TMDL reconnaissance surveys occur at sites listed in Category 5 of the most recent list of impaired water bodies (303(d) list). At this time, it is undetermined which sites will be sampled. The scope of this QAPP is broad enough to cover any additional sampling that may be necessary at any of the chosen sites. If it is determined that special sampling or analysis is needed at particular sites, the QAPP will be revised or an addendum developed to reflect that sampling.

Compliance Monitoring

The NPDES CSIs verify compliance with effluent limitations and evaluate the permittees' self-monitoring program. The program consists of 20 municipal and/or industrial inspections. The facilities scheduled for sampling are listed in Appendix B of the current CWA Sections 106 work plan.

Lake Sampling

Samples are collected as part of current work plans associated with this QAPP.

Classification of Measurements

All measurements for these programs are classified as critical. No informational purposes only samples are anticipated.

Measurement Validation Procedures

Only normal sample matrices are involved in these programs. The methods used will be EPA approved and/or current methods from *Standard Methods for the Examination of Water and Wastewater*. As such, no method validation studies are planned.

Measurement of Process Conditions

No process conditions will be measured from these program activities.

ELEMENT B2: SAMPLING METHODS REQUIREMENTS

Surface Water Samples

Samples will be collected and preserved according to the criteria in the most current EPA Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act, 40 CFR Part 136. If deviations or changes to the procedures are used, the information will be recorded in the field sampling log book.

In small streams, grab samples are collected at midstream just below the surface of the water. In large streams and rivers, a grab samples are collected at one of the quarter points from either bank just below the surface of the water. Samples are collected using a sampler designed in accordance with APHA specifications.

Dissolved oxygen, water temperature, pH, conductivity, and discharge measurements may be made on site using a meter calibrated as specified in Element B7. In occurrence of meter failure, the sampler will note the problem and take corrective actions. If unable to take corrective action, the remainder of the sampling run should be completed without that particular measurement. The meter should then be repaired or replaced prior to the next sampling event.

The collecting of dissolved metals samples will be made with a polypropylene bucket with the metal handle removed and replaced with a nylon rope. Sample and equipment blanks and duplicates are discussed in section XXX. The sample will be filtered with a disposable syringe filter into a HDPE bottle with a pre-measured amount of concentrated nitric acid. Sample bottles will be kept in a plastic zip lock bag prior to use and placed back into the bag, sealed, and placed in a plastic, compartmentalized storage unit after samples have been collected.

The qualitative flow measurement techniques established by the U.S. Geological Survey and their existing QA/QC is acceptable and will be used for these programs.

The following should be used when characterizing the "Flow Severity" at the sample site:

1 = No Flow	**4 = Flood**
2 = Low Flow	**5 = High Flow**
3 = Normal Flow	**6 = Dry**

No Flow (1) When a flow severity of one (1 = no flow) is recorded for a sampling visit, then a flow value of zero ft3/s should also be recorded for that sampling visit. A flow severity of one (1) (no flow) describes situations where the stream bed has water visible in isolated pools. There should be no obvious shallow subsurface flow in sand or gravel beds between isolated pools.

Low Flow (2) When stream flow is considered low a flow severity value of two (2) is recorded for the visit.

Normal Flow (3) When stream flow is considered normal a flow severity value of three (3) is recorded for the visit and the corresponding flow measurement should also be recorded for that visit.

Flood or High Flow (4 and 5) Flow severity values for high and flood flows have long been established by USEPA and are not sequential. Nevertheless, the flood flows should be represented by a flow severity of four (4) and high flows should be recorded with a flow severity of five (5).

Dry (6) When the stream is dry a flow severity value of six (6 = dry) is recorded for the sampling visit. This will indicate that the stream is completely dry with no visible pools.

Pesticide samples must be collected in certified, pre-cleaned (Level 2) glass containers and stored at 6°C.

A quart OR half gallon polyethylene bottle (depending on availability) is used for mineral and routine analyses collections. Nutrient samples are collected in a half gallon polyethylene bottle, preserved with H_2SO_4 to a pH < 2 and stored at or below 6°C.

The collection of bacteriological samples should be made in the stream channel approximately six inches below the surface. Sample bottles are 125mL plastic coliform bottles. If the sample must be collected from a bridge or other structure, the sample bottle is held with a stainless steel, three-prong clamp, and lowered from the bridge into the water at the mid-point of the channel. When sampling from a boat, samples are obtained from the upstream side of the boat. Samples will be stored on ice (<10C) for no more than eight hours.

Lake Sampling

The USGS field sampling protocols as outlined in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated) for the collection of grab water samples is utilized (http://water.usgs.gov/owq/FieldManual/).

The collection of water samples should be made at 1.0 meter below the surface and/or at 80% of the depth of the sample site with an alpha style, horizontal water sampler. Chlorophyll a samples should be collected from 1.0 meter below the surface and/or from just above the thermocline. The water samples will be transferred to the proper water dark plastic sampling containers and stored according to the procedures in Section B3.

A YSI-6 Series multi-parameter unit outfitted with dissolved oxygen, pH, temperature

probes, and depth sensor is utilized for profile sampling as per the methods outlined in ADEQ's "Standard Operating Procedure for Taking a Lake Profile Using a Multiparameter Sonde," 2014.

A YSI-6 Series multi-parameter unit should be deployed in mid to late summer. These monitors will be positioned as discussed on Element A6. Water-quality monitors can be secured to fishing piers or secured to poles or floats that should be anchored or driven into the bottom substrate.

Ground Water Samples

Ground water will be sampled according to recommended procedures found in the following documents in order of importance:

EPA - 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, Table A7-1.

Field measurements shall include temperature, specific conductance, and pH. Sample containers shall be in accordance with the descriptions described in the ■Surface Water Samples• section.

Macroinvertebrate Samples

Macroinvertebrate sampling will follow the protocols outlined in ADEQ's "Standard Operating Procedure for Macroinvertebrate Sampling Methodology for Wadeable Streams," (January 2014) and "Standard Operating Procedure for Macroinvertebrate Sampling Methodology for Non-wadeable Streams" (September 2012).

Fish Community Samples

Smith-Root model LR-20 and LR-24 backpack, and/or a Smith-Root GPP 5.0 electrofishing device with pulsed DC current are used to collect fish from the designated sites. The devices are used in the shallow pools and along the pool edges while wading upstream and dipping the stunned fishes from the water with dip nets. The riffles should be collected by posting a twenty foot seine near the toe of the riffle and while working the electrofisher in a downstream direction through the riffle, the bottom substrate is overturned and the fish herded or washed into the seine.

Fish species of all types are collected from all available habitats within the sample area until a fully representative sample of the species in the area is thought to be obtained. A representative sample is thought to be obtained when no new species or when no noticeable change in composition of species is noticed when collecting. This is based on professional judgment of the biologist performing the field work. Larger specimens , those approximately six inches in length, should be field identified, if possible, and released. The smaller specimens, and those unidentifiable in the field or that need further identification, should be preserved in a ten percent (10%) formalin solution and returned to the lab.

Habitat assessments are made by taking notes on each of the different habitat types encountered in the reach of the stream where fish are collected, i.e. riffle-run-pool-riffle. Notes of the length, width, depth, substrate type and microhabitat types within each habitat are taken and scored. An overall score is given to the entire collection area and comparisons between sites can be made.

For additional information, refer to ADEQs SOP for "Fish Sampling Methodology for Wadeable Streams," October 2014.

Periphyton Community Samples

Periphyton communities will be sampled at designated sites in order to quantify biomass and are addressed in the corresponding work plans. At this time, periphyton communities will not be identified to species due to high level of taxonomic expertise and time needed to complete identifications. Periphyton collections will occur during periods of stable flow, as determined by visual assessment, evaluations of hydrographs (if available), or a minimum of three weeks post-bed scouring event. Collection techniques will follow a single-habitat (riffle) approach discussed in Barbour et al. (1999). Laboratory analyses for biomass determination will include ash-free dry mass and chlorophyll a following standard methodologies (APHA 1995, USEPA 1997)

Quality Assurance Procedures for Water Sampling

Field duplicate samples and field duplicate measurements for pH, water temperature, and dissolved oxygen should be collected 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, an additional grab sample, an additional metals sample, three additional TOC samples, an additional pesticide sample, and all field measurements must be collected if they were originally collected. Metals field/equipment blanks will occur during each sampling event.

Quality Assurance for Macroinvertebrate Sampling

Quality Assurance procedures for macroinvertebrate sampling and analysis will follow the protocols outlined in ADEQ's "Standard Operating Procedure for Macroinvertebrate Sampling Methodology", April 2010.

Quality Assurance for Fish Community Sampling

Actual shocking time (Level of Effort) should be recorded in the field book and/or on the field sheet. Habitat analysis should be conducted and recorded on the fish habitat field sheet for each location (field sheets are located in the corresponding standard operating procedures) Care should be taken to sample each location of similar size for approximately the same amount of time.

Quality Assurance for Periphyton Community Sampling

Field data should be recorded on field datasheets and then recorded into working databases. A minimum of one field duplicate will be collected during each sampling event. In order to prevent sampling bias, the single-habitat sample method was selected, please refer to Barbour et al.(1999) for a detailed description. This method helps reduce sampling variability by limiting sampling to similar flow and substrate characteristics.

ELEMENT B3: SAMPLE HANDLING and CUSTODY REQUIREMENTS

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

Custody

A sample is in custody if it is in any one of the following states:

1) In actual physical possession
2) In view, after being in physical possession
3) In physical possession and locked up
4) In a secure area, restricted to authorized personnel

Sample collection

1) When possible, one sampler, referring to a person, will be used to make all samples necessary. However, all personnel doing the sampling will be trained on the sampling procedures.
2) All samples must be tagged or labeled at the time of collection. The tag or label must contain the station number and the date and time taken.
3) A chain-of-custody must accompany the samples and includes study name, collector's signature, station number and location, date, time, type of sample, and the number of containers. When turning over possession of samples, the transferor and transferee sign, date, and time the record sheet and check the sample preservation and note it on the form.
4) Field notes must be taken and contain at a minimum the same information as the sample tag and any field measurements, weather conditions, water levels, and other information necessary to reconstruct the sample collection process. All entries should be signed and all field notebooks should be stored in a safe place.
5) The sample collector is responsible for the care and custody of the samples until they are relinquished. The sample collector must provide the proper storage conditions and insure the delivery of the samples within the permitted holding times. The samples must be in his/her physical possession or in his/her view or stored in a locked place at all times. Sampling personnel are responsible for the samples until the laboratory receives custody.

Sample Shipment and Transfer of Custody

1) When samples are shipped by common carrier, a bill of lading must be obtained. This bill of lading must be retained as part of the permanent chain of custody.
2) Samples delivered to other personnel must be accompanied by a chain of custody. This consist of a "relinquished by" and "received by" signatures on the chain of custody form.

3) Samples must be delivered to authorized personnel and the transfer of custody recorded by signatures, date, and time of the transferor and transferee.
4) Environmental Preservation/Technical Services Division chemists and the Division Chief are authorized to receive samples in the laboratory.

Laboratory Custody

1) The chemist supervisor or designee shall be the Sample Custodian. The Sample Custodian 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 Sample Custodian's absence, a substitute will be designated.
2) Samples received in the laboratory shall be recorded in a laboratory information management system (LIMS), with the sample description, date and time collected, name of collector, the date and time received, and the person receiving the sample.
3) The laboratory personnel are responsible for the care and custody of a sample once it is handed to them and should be prepared to testify that the sample was in their possession and view or secured in the laboratory at all times.
4) The laboratory area shall be maintained as a secured area and shall be restricted to authorized personnel.
5) All analyses must be completed within the approved holding times as outlined in the most current ■40 CFR Part 136 - Guidelines Establishing Test Procedures for the Analysis of Pollutants.•
6) 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.
7) Samples should be destroyed only upon the order of the chemist supervisor, in consultation with the sampler.

Biological Samples

1) The macroinvertebrate samples should be labeled at the time of collection. The labels should have the sample site, date of sample, samplers names, and project name clearly printed on them. Each sample should be preserved in a tightly sealed glass or plastic container labeled both internally and externally.
2) The fish community samples should be labeled at the time of collection. The label should have the sample site, date of sample, and project name clearly printed on them. Each sample should be preserved in a tightly sealed plastic container with the label attached or written directly onto the container.
3) Periphyton community samples should be labeled at the time of collection. The label should have the sample site, date of sample and project name clearly printed on them. Each sample should be preserved in a tightly sealed plastic container with the label attached or written directly onto the container.
4) Duplicate information should be recorded into the field book along with any field measurements collected and the duration of the sample event.
5) The sampler is responsible for accomplishing all of the above steps and is also responsible for the safe transfer and storage of the samples to and at the ADEQ.

ELEMENT B4: ANALYTICAL METHODS REQUIREMENTS

Analytical procedures must be referenced in the most current Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act; 40 CFR, Part 136 except the following; Some Metals by EPA Method 200.8, Volatile Organic Compounds by GC/MS, SW-846 Method 8260C Rev. 3, 8/2006, Semi-volatile Organic Compounds by GC/MS, SW-846 Method 8270D Rev. 4, 2/2007,Pesticides by EPA Method 525.1. Table B4-1 lists the equipment used to perform the following procedures.

Physical

1. Conductivity, µmhos, Standard Methods, Method 2510 B-1997.
2. Temperature, degrees C, calibrated glass thermometer, Standard Methods, , Method 2550 B-2000.
3. Turbidity, Nephelometric Turbidity Units, Nephelometric, Standard Methods, , Method 2130 B-2001.

Residue

1. Total dissolved, mg/l, glass fiber filtration 180° C gravimetric, Standard Methods,, Method 2540 C-1997.
2. Total suspended, mg/l, glass fiber filtration 103-105° C gravimetric, Standard Methods, Method 2540 D-1997.

Mineral

1. Chloride, mg/L, Ion Chromatography, EPA, Method 300.0
2. Sulfate, mg/L, Ion Chromatography, EPA, Method 300.0
3. Fluoride, mg/L, Ion Chromatography, EPA, Method 300.0
4. Bromide, mg/L, Ion Chromatography, EPA, Method 300.0

Miscellaneous

1. Dissolved Oxygen, mg/L, Electrode, Standard Methods, , Method 4500-O G-2001.
2. Hardness-total as CaCO3, mg/L, by calculation, Standard Methods, , Method 2340 B-1997.
3. Hydrogen ion (pH), pH units, electrometric measurement, Standard Methods, , Method 4500-H^+ B-2000.

Demand Analysis

1. Biochemical Oxygen Demand-5 day, mg/L, Electrode method, Standard Methods, Method 5210 B-2001.
2. Carbonaceous Biochemical Oxygen Demand-5 day, mg/L, Electrode method, Standard Methods, Method 5210 B-2001.
3. Total Organic Carbon, mg/L, Persulfate-Ultraviolet Method, Standard Methods, Method 5310 C-2000.

Table B4-1: LABORATORY ANALYTICAL EQUIPMENT

Equipment	Parameter
Sartorius MSA 124S-100-DI Balance	Total Dissolved Solids, Total Suspended Solids
Yamato DKN602C; Lindberg Blue Oven	Total Dissolved Solids, Total Suspended Solids
Thermometer	Temperature
YSI Model 5100, 57, 550A	Dissolved Oxygen
Orion Model EA920, 210, 230A	pH
Orion Model 1230	Conductivity
Lachat Model QuickChem 8500 Series 2	NH_3-N, NO_2+NO_3-N, Orthophosphorus, Total Phosphorus, TKN, Alkalinity
Dionex Model ICS 1000 IC	Chloride, Sulfate, Bromide, Fluoride
Sievers 5310C	Total Organic Carbon
Agilent 7890A GC with 240 ion trap MS	SemiVOCs, Pesticides
Shimadzu GC 2010 plus AE	PCBs, Chlordane, DRO, GRO
Varian Saturn 3800/4000 GC/MS	VOC,
Thermo ICP/MS Model X7	Total Hardness (Calculated), Aluminum, Barium, Beryllium, Boron, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Nickel, Potassium, Sodium, Vanadium, Zinc
H.F. Instruments Model Micro 100	Turbidity
Trilogy Laboratory Fluorometer	Chlorophyll a
Millipore Test Manifold, UV Sterilizer, Dual Chamber Incubator	Bacteria, Fecal Coliform, *Escherichia coli*

Nutrients

1. Ammonia, as nitrogen, mg/L, automated phenate, Standard Methods, Method 4500-NH3 H-1997.
2. Nitrite + Nitrate, as nitrogen, mg/L, automated cadmium reduction, Standard Methods, Method 4500-NO_3^- F-2000.
3. Kjeldahl Nitrogen, as nitrogen, mg/L, digestion using SM 4500-P, J-1999 followed by analysis using Standard Methods, Method 4500-NO_3^- F-2000.
4. Ortho-phosphorus, as phosphorus, mg/L, automated ascorbic acid, Standard Methods, currently approved editions, Method 4500-P, G-1999.

5. Total Phosphorus, as phosphorus, mg/L, persulfate digestion followed by automated ascorbic acid, Standard Methods, Methods 4500-P, G-1999.
6. Chlorophyll a, µg/l, EPA Method 445.0.

EPA Method 200.8 Rev. 5.4 (ug/L)			
Aluminum	Boron	Arsenic	Nickel
Antimony	Calcium	Cadmium	Selenium
Barium	Silica Dioxide	Chromium	Silver
Beryllium	Sodium	Cobalt	Thallium
		Copper	Titanium
		Lead	Vanadium
		Molybdenum	Zinc

Metals Analysis

1. Total Metals are analyzed after preliminary digestion using EPA Method 200.2, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements or SW 846-3015, Closed Vessel Microwave Digestion.
2. Digestion for all metals analysis EPA/600/R-94/111 May 1994, Method 200.2
3. Dissolved Metals are analyzed after filtration at the time of collection using a 0.45Φ filter followed by acidification to a pH of <2 using nitric acid.
4. EPA Method 200.8, Rev. 5.4, (1994) is used for total-dissolved metals analysis.

Volatile Organic Components

Volatile Organic Compounds are analyzed by GC/MS, SW-846 Method 8260C Rev. 3, 8/2006

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
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

Semivolatile organic compounds are analyzed using EPA Method 8270D Rev. 4, 2/2007

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
Compound	**CAS Number**	**Compound**	**CAS Number**
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
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

Pesticide compounds are analyzed by EPA method 525.1

Compound	CAS Number	Compound	CAS Number
1,4-Dichlorobenzene-d4 (IS)		Fonofos	944-22-9
Naphthalene-d8 (IS)		Delta-BHC	319-86-8
Acenaphthene-d10 (IS)		Cyprazine	22936-86-3
Phenanthrene-d10 (IS)		Dimethazone	81777-89-1
Chrysene-d12 (IS)		Metribuzin	21087-64-9
Nitrobenzene-d5(Surr.)		Methyl-Parathion	298-00-0
2-Fluorobiphenyl(Surr.)	321-60-8	Alachlor	15972-60-8
Terphenyl-d14(Surr.)	1718-51-0	PCB-as-AR1242	53469-21-9
2-4-6-Tribromophenol(Surr.)	118-79-6	PCB-as-AR1248	12672-29-6
PCB-as-AR1221	11104-28-2	Ametryn	834-12-8
PCB-as-AR1232	11141-16-5	Prometryn	7287-19-6
Molinate	2212-67-1	Heptachlor	76-44-8
Propachlor	1918-16-7	Terbutryn	886-50-0
Trifluralin	1582-09-8	Malathion	121-75-5
Alpha-BHC	319-84-6	Dipropetryn	4147-51-7
Atraton	1610-17-9	Metolachlor	51218-45-2
Prometon	1610-18-0	Chlorpyrifos	2921-88-2
Simazine	122-34-9	Cyanazine	21725-46-2
Atrazine	1912-24-9	Aldrin	309-00-2
Beta-BHC	319-85-7	Pendimethalin	40487-42-1
Propazine	139-40-2	Heptachlor-Epoxide	1024-57-3
Gamma-BHC	58-89-9	Procyazine	32889-48-8
Compound	**CAS Number**	**Compound**	**CAS Number**
Terbuthylazine	5915-41-3	Technical-Chlordane	57-74-9
Diazinon	333-41-5	Endosulfan-I	959-98-8
Fluchloralin	33245-39-5	p-p'-DDE	72-55-9
Dieldrin	60-57-1	Endosulfan-Sulfate	1031-07-8
Endrin	72-20-8	p-p'-DDT	50-29-3
PCB-as-AR1254	11097-69-1	Hexazinone	51235-04-2
PCB-as-AR1260	11096-82-5	Norflurazon	27314-13-2
Endosulfan-II	33213-65-9	Endrin Ketone	53494-70-5
p-p'-DDD	72-54-8	Methoxychlor	72-43-5
Endrin Aldehyde	7421-93-4		

Bacteriological

1. Fecal Coliform, number per 100 mL, membrane filter, Standard Methods, Method 9222 D-1997
2. Total Coliform, number per 100 mL, membrane filter, Standard Methods, Method 9222 B-1997.
3. *E. coli*, number per 100 mL, membrane filter, EPA Method 1603, 12/2009.

Decontamination and Waste Disposal

No decontamination waste will be generated. All waste solvents generated by extraction procedures used are collected and recycled by a hazardous waste treatment facility.

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. The Incident Report Form (IRF) should be used 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 IRF should be sent to the QA Officer and Lab Supervisor. The QA Officer and/or Lab Supervisor must sign off on any data that must be voided or coded.

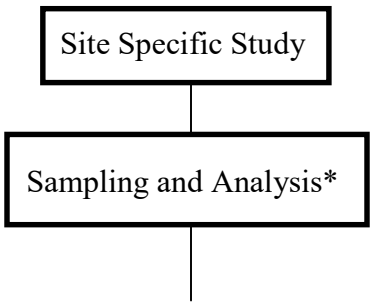
Problems with the samples should be documented on the Incident Report Form and the QA officer should contact the sampler. Corrective actions will include training and communication of sampling requirements.

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial Instrument Blank	Response < MDL	Prepare another blank, determine cause
Initial Calibration	COV > 0.995	Reanalyze standards, make new standards
QC Check Standard	Method or lab established	Reanalyze, prepare new QC check

	limits	standard
Continuing Calibration	Method Limits	Recalibrate and reanalyze samples
Sample Duplicates	Precision within Limits	Reanalyze, qualify results
Matrix Spike Duplicates	Precision within Limits	Reanalyze, determine cause, qualify results
Matrix Spike Duplicates	Recoveries 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	≤ 6°C	Adjust refrigerator Temperature

Macroinvertebrates

Matrices set forth in Rapid Bioassessment Protocols for Use in Stream and Rivers (EPA/444/4-89-001, 1989) may be used in the analysis of the macroinvertebrate samples. Some of these matrices include, but are not limited to; 1) Taxa Richness, 2) Quantitative Similarity Index - Taxa, 3) Ephemeroptera-Plecoptera-Tricoptera Index, (EPT) 4) Hilsenhoff Biotic Index, 5) Percent Dominant Contribution, 6) Scraper/(Filterer + Scraper) abundances, 7) EPT/(EPT + Chironomidae) abundances, and 8) Quantitative Similarity Index - Functional Groups.



Metric	Biological Condition Scoring Criteria 6	4	2	0
Taxa Richness [a]	>80%	60-80%	40-60%	<40%
Hilsenhoff Biotic Index [b]	>85%	70-85%	50-70%	<50%
Ratio of EPT to Chironomid Abundances [a]	>75%	50-75%	25-50%	<25%
% Contribution of Dominant Taxa [c]	<20%	20-30%	30-40%	>40%
EPT Index [a]	>90%	80-90%	70-80%	<70%
Community Loss Index [d]	<0.5	0.5-1.5	1.5-4.0	>4.0

a) Score is a ratio of study site to reference site X 100
b) Score is a ratio of reference site to study site X 100
c) Scoring criteria evaluate actual percent contribution, not percent comparability to reference site
d) Range of values obtained. A comparison to the reference site is incorporated in these indices.

*Modified from Plafkin, J.L. M.T. Barbour, K.D. Porter, S.K. Gross, and R.M. Hughes. 1989. Rapid bioassessment protocols for use in streams and rivers: Benthic macroinvertebrates and fish. U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington D.C. EPA 440-4-89-001.

A total score consisting of the community analysis and the physical habitat analysis is calculated for each sample and sample site. The ratio between the sample site and the reference site provides the percent comparability for each station. The percent comparability categories are:

Attainment Status	% Comparable Estimate (%CE)	Attribute
Comparable to reference	≥90%	Expected to support the community structure present at the reference site.
Supporting	75-88%	Should support a diverse community similar to the reference site.
Partially Supporting	60-73%	Difference in the biological community may be due to the poor habitat. Comparisons may be difficult.
Non-supporting	<58%	Should not be expected to support the community present at the reference site.

Each site will have a RBA (Rapid Bioassessment) score derived from multi-metric analysis, as described above, and compared to the reference site score to determine the impairment status of the site. The impairment categories are:

Impairment Status	% Comparable Estimate (%CE)	Attribute
No Significant Impairment	>83%	Comparable to the best situation to be expected. Balanced trophic structure and optimum community structure present.
Slight Impairment	54-79%	Community structure less than expected. Taxa richness lower than expected. Some intolerant taxa loss. Percent contribution of tolerant forms may increase.
Moderate Impairment	21-50%	Obvious decline in taxa richness due to the loss of tolerant forms. Reduction in the EPT index.
Severe Impairment	<20%	Few taxa present and normally dominated by 1 or 2 taxa.

Fish Community

Larger specimens easily identified should be field identified and released. Smaller specimens, and those needing closer examination, should be returned to the lab for better identification. Ichthyological taxonomic keys of Douglas, Pflieger, and Buchanan may be used to speciate the collected specimens.

Direct comparisons to either; 1) upstream/downstream fish community data, 2) ecoregion fish community data (Appendix 4), or 3) least-disturbed reference stream data may be used to analyze the data. Percent community on the species, generic, and family levels will also be employed. In addition, the Shanon-Weaver, and Odums diversity indices, as described in the "Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses", EPA, November 1983, may be used in analyzing the data. In addition, best profession judgment may be employed for those samples that the metrics are unable to evaluate. This may occur when a sample site is within a transition zone between two ecoregions, or when there is a large number of one species, usually young-of-year, because of a recent hatch.

The ecoregion fish community metrics were established utilizing information from the 1987 ecoregion survey (ADPC&E 1987) and supplemented with data from additional least-disturbed streams identified by ADEQ personnel. A group of Arkansas ichthyologists reviewed the data and utilizing the prevailing deviations in the data set and employing best professional judgment, established the current metric scores and similarity rankings categories.

Periphyton Community

Biomass metrics for periphyton are limited and have used little among state and federal regulatory agencies due to results that are often interpreted as ambiguous. This is often due to the potential influence from scour events, toxicity, or heavy grazing (Barbour et al. 1999). Data collected may be used as baseline information until a large enough dataset exists to determine mean and maximum biomass concentrations.

ELEMENT B5: QUALITY CONTROL REQUIREMENTS

Sampling

Field duplicate samples and field duplicate measurements for pH, water temperature, and dissolved oxygen should be collected 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, an additional grab sample, an additional metals sample, three additional TOC samples, an additional pesticide sample, and all field measurements must be collected if they were originally collected.

Laboratory

The quality of data from the laboratory will be assured by a system of internal checks. These include equipment checks, reagent checks, and laboratory performance checks. The results will be recorded to verify the quality control system and to monitor any changes that occur.

Chemical Laboratory

1. Each day before use, all analytical balances must be checked for calibration using a series of NIST traceable weights demonstrating the range of the balance (1 g, 20 g, 50 g, and

100 g). The balance reading for each weight must be within a range of acceptability for the balance to meet calibration check requirements. If any balance reading falls outside of the range of acceptability, the balance must be calibrated. The range of acceptability is calculated 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 SD.

2. The temperature of BOD incubator is recorded automatically twice daily at twelve hour intervals by a datalogger. The temperature must be 20 +/- 1.0 °C at all times. Corrective action, adjustment or repair must be taken if this temperature range is not met.
3. The temperature of all residue drying ovens must be recorded at the beginning and end of the drying cycle and recorded on the 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. Corrective action, adjustment, or repair must be taken if these temperatures are not correct.

4. The results of each pH calibration must be recorded in the pH calibration log book. If the electrode response to two buffers shows differences greater than 0.1 pH unit, corrective action must be taken. If recalibration, cleaning the electrodes, or changing the buffers does not solve the problem, the electrodes may have to be replaced.

Bacteriology Laboratory

1. Thermometers
   A. Calibrate annually against a NIST traceable thermometer in the monitoring range in which thermometer will be used.

2. Dual-Chamber/Portable Incubator
   A. Maintain at 35EC. or 44.5 EC (±0.2 EC), depending on sample requirements.
   B. Record temperature of incubator on sheet at beginning and end of testing.
3. Autoclave
   A. Place a minimum/maximum recording thermometer, with its bulb immersed in water, in the center of each autoclave load. Shake the thermometer down prior to placement in load. Following cycle record maximum temperature in Bacteriology Temperature Control Log Book.
   B. Record pressure and autoclave cycle time in Bacteriology Temperature Control Log.
   C. A sterilization indicator strip is placed inside the autoclave prior to operation. A change in color of the strips indicates sterilization is complete. If the strip does not change in color the sterilization was incomplete. Identify the cause of incomplete sterilization and correct it prior to the next sterilization cycle. Record corrective procedures in the Bacteriology Quality Control Log Book.
4. Membrane Filtration Equipment
   A. To sterilize funnels and bases, expose to ultraviolet light in the ultraviolet sterilizer for 2 minutes. Re-sterilize funnels following each sample filtration.

C. Check funnels for leakage and replace washers when necessary.

5.

6. Laboratory Glassware

A. Use sterile, disposable pipettes only. Glassware used for media preparation is washed in dishwasher using a phosphorus-free detergent and rinsed with deionized water. Foil covers are placed over openings of glassware. Glassware is then placed in a drying oven at 170°C for a minimum of 1 hour.

7. Laboratory Pure Water:

A. Deionized water is monitored for conductance, NH3-N, and NO3+NO2-N; cadmium, chromium, copper, selenium, zinc, and arsenic by its use in the preparation of method blanks.

B. Specific conductance results should not be greater than 0.2 megohm resistivity or less than 5.0 microohms/cm.

C. A method blank is also prepared for each batch of micro samples analyzed..

. 8. Rinse and Dilution Water

Prepare buffered water according to procedures.

9.

10. Membrane Filters and Pads

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A. Aseptically place an uninoculated membrane filter onto an absorbent pad or agar surface at the beginning and ending of each sample series. Incubate at the correct time and temperature. Growth on the membrane filter indicates contamination of the filter. The cause should be identified and corrected.

B. Incubate a saturated absorbent pad or agar plate at the correct time and temperature. Growth on the pad or plate indicates the media is contaminated and the cause of contamination should be identified and corrected.

. 11. Media

A. Maintain an inventory record of media including date received, amount, number of units received, and date opened.

B. Discard opened bottles of media when caking of the media begins to occur.

C. Maintain a prepared media record including amount of media prepared, sterilization time and temperature, final pH of media, and preparer's initials.

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12. Analyst Precision and Accuracy

A. Conduct duplicate analyses on ten percent of all samples.

B. Determine the upper control limit of duplicates.

C. A negative control (method blank) and a positive control (known reference standard) are analyzed for each batch of up to 20 micro samples analyzed.

13. Rejection of Bacteriological Samples

A. Special bacteriological samples should be delivered to the laboratory within six hours of collection and all samples shall be plated and incubated within eight hours of collection time. Chain of custody sheets should accompany all samples.

B. Bacteriological samples collected in bottles other than sterilized borosilicate glass or sealed, plastic bacteriological sample bottles, shall be rejected.

C. Bacteriological samples shall be preserved at 4 °C, in 0.008% $Na_2S_2O_3$.

Laboratory Performance Checks

The performance of the laboratory will be checked using duplicate field samples duplicate matrix spiked samples, laboratory control spiked samples, and check samples from an outside source. See numbered bullets below for type and frequency of each.

1. All chemical analyses possible will be checked for accuracy by the analysis of Laboratory Control Samples (LCS). A minimum of one LCS will be analyzed per batch of twenty samples. These spike samples will be prepared by the addition of a known amount of target analyte(s) to an aliquot of de-ionized water, free of target analytes and organics. The LCS recoveries will be compared to method or lab generated acceptance criteria. The results must be entered in the LIMS QC system and verified to be within the control limits.
2. Laboratory precision and the effects of the matrix on analyte recovery will be 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. The precision and recoveries of the MS/MSD will be compared to method or lab generated acceptance criteria. The results must be entered in the LIMS QC system and verified to be within the control limits
3. Check samples from an outside source will be analyzed semi-annually. Proficiency testing (PT) samples are provided by USGS or purchased from a TNI (The NELAC Institute) approved vendor. The expected values of the PT samples is unknown to the analyst at the time of analysis.
4. Bacteriological analyses will be checked for precision by the analysis of duplicate samples. Duplicate samples will be collected in the field by the person or team collecting the sample. A positive control (a known reference standard) and a negative control (method blank) are also analyzed per analytical batch of no more than twenty samples. These controls demonstrate the efficiency of the analytical process and the absence of contaminants or interferences .

1.

Procedures to Assess Data Precision and Accuracy

The precision and accuracy of all laboratory data will be assessed immediately after the analyses are performed. The data from all duplicate and spiked samples will be entered into a computer system which will plot the data, check it against the acceptance criteria, and check for violations. The system will keep the acceptance criteria used for that sample. New acceptance criteria will be generated in December and July using the data from the previous six months.

1. Precision
   A. The precision of the data will be determined from field duplicate samples and laboratory spiked replicate samples.
   B. The control limits for precision will be determined by either method specified or historical data. Outlier data will be discarded before calculations are made. A series of control limits will be determined for different concentration ranges when necessary.

Field Precision

Field precision will be based on the relative percent difference between the sample and its field duplicate.. The control limits will be based on laboratory established limits. The RPD will be calculated as follows:

RPD = ({Duplicate – Original}/{(Duplicate + Original)/2})*100

Laboratory Precision

The values from laboratory spiked replicate samples will be used to evaluate laboratory precision. The control limits will be based on method control limits or lab established limits.

The RPD will be calculated:

RPD = {Duplicate – Original}/{{Duplicate + Original}/2}*100

2. Accuracy

The control limits for accuracy are based on method or lab established limits and will be be based 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

The analysis will be considered out of control the percent recovery of the LCS is outside of the acceptance criteria for that parameter..

3. 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:

A. Quality control checks reveal a problem
B. The QC data is out of control.
C. Deficiencies are cited during an audit.
D. Data is determined to be questionable by an outlier test.

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
Trip blanks	< Reporting limit	For common volatile contaminants (e.g. methylene chloride) the trip blanks are allowed to have 5X the reporting limit. The presence of any detected target analyte is reported; all samples positive for this target analyte will be flagged by a qualifier meaning "analyte is present in the trip blank.".
Laboratory Control Sample (LCS)	% recovery within method specified OR laboratory established limits	Check spiking solution; re-prep LCS and re-analyze LCS with associated samples.

Duplicates And Matrix Spikes

Duplicate Type	Corrective Action
Field Duplicates	Reanalyze samples. If samples are still out of control, flag the data from sampling event. Document on incident report.
Matrix Spikes/Matrix Spike Duplicates	Reanalyze samples. Check spike solution. Check for matrix interferences. Document on incident report. Qualify affected samples.

Acceptance Criteria and Corrective Actions for Performance Evaluation Samples

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

1. Checking calculations and data transcription.
2. Checking calibration and calibration standards.
3. Investigation of possibility of analyst error or improper technique.
4. Investigation of possibility of instrument malfunction.
5. Investigation of possibility of matrix interference.
6. Documentation of Corrective Actions

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

4. Representativeness

Determining whether the results from a sample represent the true values in the stream being sampled are controlled by the sampling process. Site selections will be the responsibility of the Project Manager. Sampling procedures and training of the samplers will be the responsibility of the Field Coordinator. The actual representativeness will be assessed from the field duplicates. The control limits set for each field duplicate parameter are meant to assure proper sampling techniques.

5. Comparability

A. Analytical methodology. EPA approved methods and/or current methods from *Standard Methods for the Examination of Water and Wastewater,* will be used. All data generated will be entered into the EPA STORET data system with the appropriate parameter code and with the standard units.

B. Performance Evaluation Samples. The laboratory will participate in two performance evaluation studies annually provided by the U.S. Geological Survey. Also, two performance evaluations from an TNI (The Nelac Institute) approved performance evaluation provider will be conducted annually. These studies document the laboratory's ability and compare our results with other laboratories throughout the country.

6. Completeness

The work plan for monitoring lists all of the stream stations and CSI sites for the year with the sampling frequency. A quarterly report of the number of samples collected is made to the Project Manager. A Midyear Status report and an End of Year report, incorporating the percent of samples collected and analytical results generated, is prepared for the Project Manager.

ELEMENT B6: INSTRUMENT MAINTENANCE REQUIREMENTS

Inspections and Acceptance Testing of Instruments

All instruments purchased for this project will 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 and/or as per manufacturers' recommendations or operating instructions.

Final Acceptance

The final acceptance will be performed by the Chemist Supervisor to assure compliance with purchase requirements.

Resolution of Deficiencies

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

Preventive Maintenance

1. Analytical Balance
   A. All analytical balances must be cleaned weekly and immediately after any chemical spills.
   B. The balance table must be kept neat and cleaned after any spills. Any spill that might interfere with trace analysis, such as mercury compounds, must be immediately and thoroughly cleaned up.
   C. All analytical balances must be cleaned and checked by a balance service annually or whenever a problem is found.

2. Dissolved Oxygen Meters
   A. The membrane on the probe should be changed whenever the response is sluggish or erratic.
   B. The following spare materials should be maintained on hand:
      1. membranes
      2. filling solution
      3. O-rings
      4. batteries
      5. electric motor for stirrer

3. pH Meter
   A. The pH electrodes should be maintained by following the manufacturer's recommendations for electrolyte solutions and storage procedures.
   B. The following spare materials should be maintained on hand:
      1. glass electrode or combination electrode
      2. reference electrode
      3. electrolyte solutions
      4. pH 4, 7, and 10 buffer

4. Conductivity Meters
   Conductivity cells should be cleaned and replatinized whenever the readings become erratic, when a sharp endpoint cannot be obtained, or when inspection shows fouling or that any of the platinum black has flaked off.

5. Lachat Model QuickChem 8500 Series 2
   A. The preventive maintenance schedule for the sampler, pump, and colorimeter will be performed as per manufacturer's recommendations.
   B. The following spare materials should be maintained on hand:
      1. Pump Tubes
      2. Teflon tubing
      3. O-rings
      4. Transmission Tubing

6. Dionex Model ICS 1000
   A. The preventive maintenance schedule for the Dionex Model ICS 1000 ion chromatograph will be performed as per manufacturer's recommendations.
   B. The following spare materials should be maintained on hand:
      1. column #046124
      2. guard column #046134
      3. replacement frits

7. Sievers 5310C
   The preventive maintenance for the Sievers 5310C TOC analyzer will be performed as per manufacturer's recommendations.

8. Varian Saturn 3800 and 4000 Gas Chromatograph/Mass Spectrometers
   A. The preventative maintenance schedule for the Gas Chromatograph/Mass Spectrometer will be performed as per manufacturer's recommendations.
   B. The following spare materials should be maintained on hand:
      1. Filaments
      2. carrier gas (special order)
      3. Septa
      4. vacuum pump oil
      5. molecular sieve

9. Thermo ICP/MS Model X7
   A. The preventative maintenance schedule for the Thermo ICP/MS Model X7 will be performed as per manufacturer's recommendations
   B. The following spare materials should be maintained on hand:
      1. Pump tubing
      2. Inline filters
      3. Nebulizer PN QM006

10. H. F. Instruments Model Micro 100

A. Cuvettes must be clean and free of rubs or scratches in the critical area. Cuvettes must be cleaned by washing in a detergent solution then thoroughly rinsed with distilled water.

B. The following spare materials should be maintained on hand:
   1. light source 2. sample cell

11. Trilogy Laboratory Fluorometer
   A. The preventive maintenance schedule for the fluorometer will be performed as per manufacturer's recommendations

12. Ultraviolet Sterilizer
   Four ultraviolet bulbs should be maintained on hand to replace burned out bulbs.

13. Deionized Water Unit
   A. The ion exchange cartridges and filters for the DI water system will be changed whenever the resistance of the DI water drops below one megohm.
   B. The following spare materials should be maintained on hand:
      1. Cartridges and filters

ELEMENT B7: CALIBRATION 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. Field instruments are calibrated prior to use and individual calibration logs maintained. Multi-parameter Sondes are calibrated before and after multi-day deployments. Calibration procedures are used on the following equipment.

1. Instrumentation
   A. Laboratory Balances

      1. Sartorius Model CP124S
      2. Mettler Model AE200
      3. Mettler Model PB 303S
      4. Fisher Scientific accu-4102
      5. Sartorius Model MSA124S-100-DI

   B. General Equipment
      1. YSI Models 5100, 57 and 550A Dissolved Oxygen meters
      2. Orion Models EA920, 210 and 230A pH ISE meter
      3. Orion Model 1230 Conductivity meter
      4. Lachat Model QuickChem 8500 Auto Analyzer with IC module
      5. Dionex ICS 1000 Ion Chromatograph
      6. Sievers Model 5310C Total Carbon Analyzer
      7. HF Instruments Model Micro-100 Turbidimeter
      8. Trilogy Laboratory Fluorometer

   C. Organics
      1. Varian Models Saturn 3800 and 4000 GC/MS/DS with autosampler
      2. Tekmar Atomx purge and trap with autosampler
      3. Agilent Model 1100 HPLC with variable UV-Vis and fluorsecence detectors
      4. Shimadzu GC 2010

   D. Metals
      1. Thermo ICP/MS Model X7
      2. CEM Model 2100 microwave digestion system
      3. Leman Labs Hydra AF Mercury Analyzer

2. Stock Standard Receipt and Traceability
   A. Purchased Standards
      Stock standards should be purchased from reputable vendors. They should be National

Institute of Standards and Technology traceable, and be labeled with a lot number and an expiration number. Certificates of analysis should be filed for future reference.

B. Prepared Standards
Standards prepared from pure compounds should be documented in the standard preparation logbook for traceability. This information should include: manufacturer; lot number; expiration date; weights and volumes taken; final concentration; and preparers initials

C. Intermediate Standards and Spiking Solutions
The preparation of intermediate dilutions, mixed standards and spiking solutions must be recorded in the standard preparation logbook. 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.

3. Calibration Standards
Calibration standards are prepared from stock or intermediate standards. The preparation of the standards must be documented in the standard preparation logbook. 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.

4. Instrument Calibration
All instruments and equipment will be calibrated according to the manufacturers' recommended procedures and the guidelines in the Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019. The following specific procedures will be followed:

A. Analytical Balance, Sartorius Model MSA124S-100-DI
The balance is serviced and calibrated annually by an outside contractor. Each day before use, the balance must be checked for calibration by using a set of class NIST traceable weights. The readings for the weights must be entered in the balance check worksheet. The acceptance criteria for the calibration are based on historical data.

B. Thermometers
All thermometers will be checked against a NIST-traceable thermometer before use and annually. The check should be performed in the range of temperatures for which the thermometer is used.

C. DO Meters
1. For air calibration, place the probe in a BOD bottle containing 1 inch of water to provide a 100% relative humidity environment.
2. Allow the probe to polarize and the temperature to stabilize for at least 15 minutes.
3. Make sure the readings are stable, then press the auto-calibrate key to calibrate.
4. Air saturate a volume of water by aerating for at least 15 minutes at a relatively constant temperature. Place the probe in the aerated water and provide adequate stirring. The DO reading must be at least 98% saturated.

D. pH Meters
Initial Calibration: The meter is standardized with the pH 7 buffer and the pH 4 buffer. Read the pH 10 buffer and record the readings for all three buffers in the calibration log book along with the date, time and lot numbers for the buffers used.

E. Conductivity Meter, Orion Model 1230
The conductivity meter must be calibrated before each use by determining the cell constant. The cell constant should be determined by measuring the resistance of a 0.01 M
KCl solution. Four portions of 0.01 M KCl solution should be adjusted to 25.0 +/- 0.1°C in a water bath. The conductivity cell should be rinsed in the first three portions and the resistance, R, of the fourth portion should be measured. The cell constant is calculated by: $C = R_{KCl} \times 0.001413$.

F. Lachat Model QuickChem 8500 Series 2 Autoanalyzer with IC module
1. The initial calibration is a 7 point standard curve of the analyte. Any sample results greater than the highest standard in the calibration curve will be diluted to be within the linear curve.
2. The data system performs a mathematical fit of the standards. The correlation coefficient must be > 0.995
3. An initial calibration verification (ICV) sample is run to check accuracy of the calibration. The ICV must be from a different source than the calibration standards. The results of the ICV must be within the acceptance criteria.
4. A continuing calibration verification (CCV) standard determines the initial value.
5. Analyze 10 samples
6. Analyze continuing calibration standard. Check results for acceptance criteria.
7. Analyze 10 samples.
8. Repeat steps 6 and 7 through entire run
9. If the ICV or the CCV results fails the criteria the initial calibration must be repeated and the samples analyzed since the last successful CCV must be reran.

G. Dionex Model ICS 1000
1. The initial calibration is a 7 point standard curve of the analyte. Any sample results greater than the highest standard in the calibration curve will be diluted to be within the linear curve.
2. The data system performs a mathematical fit of the standards. The correlation coefficient must be > 0.995
3. An initial calibration verification (ICV) sample is run to check accuracy of the calibration. The ICV must be from a different source than the calibration standards. The results of the ICV must be within the acceptance criteria.
4. A continuing calibration verification (CCV) standard determines the initial value.
5. Analyze 10 samples
6. Analyze continuing calibration standard. Check results for acceptance criteria.
7. Analyze 10 samples.
8. Repeat steps 6 and 7 through entire run

9. If the ICV or the CCV results fails the criteria the initial calibration must be repeated and the samples analyzed since the last successful CCV must be reran.

H. Sievers Model 5310C Total Organic Carbon Analyzer
Follow the same procedures for the Dionex Model ICS 1000.

I. Varian Saturn 2000 and 4000 Gas Chromatograph /Mass Spectrometer. The instrument will be autotuned and mass calibrated using FC43 according to the manufacturer's recommendations. Next, method tuning criteria must be met using a 20 ng injection of 4-Bromofluorobenzene (BFB) for volatile organics or decafluorotriphenylphosphine (DFTPP) for semivolatile organics. A background-corrected mass spectrum must meet all of the key M/Z criteria for the method being used. If all of the criteria are not met, the analyst must troubleshoot the mass spectrometer and/or modify the analytical method. Then repeat the test until all criteria are achieved. These criteria must be demonstrated during each 12 hour shift.

A. Initial Calibration. A minimum of five calibration standards must be prepared. One of the calibration standards should be at a concentration near, but above, the detection limit. The others should correspond to the range expected in the samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for the method. The response factors for each compound must have a percent relative standard deviation of less than 30%.

A system performance check must be performed to ensure that minimum average Response Factors (RFs) are met before the calibration curve is used. The System Performance Check Compounds ((SPCCs)) to be checked are listed in the method.

2. Daily Calibration. A mid-concentration standard containing each compound of interest, including all required surrogates, must be analyzed every 12 hours. The SPCC compounds must meet the minimum RFs. If the SPCC compound pass then the Calibration Check Compounds (CCCs), listed in the method, are used to check the validity of the initial calibration. If the percent difference for each CCC is less than 30% the initial calibration is assumed to be valid.

J. Thermo ICP/MS Model X7

1. Pre-calibration routine - The following precalibration routine must be completed prior to calibrating the instrument until such time it can be documented with periodic performance data that the instrument meets the criteria listed below.

Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 minutes for instrument warm up. During this process conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. For proper performance, adjust resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

Instrument stability must be demonstrated by running the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

Internal Standardization - Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application, detail the use of five internal standards; scandium, yttrium, indium, terbium and bismuth. These were used to generate the precision and recovery data attached to this method. Internal standards must be present in all samples, standards and blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank or sample solution, or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a concentration range of 20-200 µg/L of each internal standard is recommended. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

2. Calibration - Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated using one of the pre-calibration routines described above. The instrument must be calibrated for the analytes to be determined using the calibration blank and calibration standards prepared at one or more concentration levels. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

   The rinse blank should be used to flush the system between solution changes for blanks, standards and samples. Allow sufficient rinse time to remove traces of the previous sample (EPA Method 200.8 Rev 5.4). Solutions should be aspirated for 30 seconds prior to the acquisition of data to allow equilibrium to be established.

K. HF Instruments Model 100 Turbidimeter

The turbidimeter must be checkcheckedcheck for calibration before each use using certified turbidity standards purchased from a vendor. If the NTU readings for any of the standards fall outside the acceptance criteria, the meter is re-calibrated using standards of 1000, 10, and 0.02 NTU.

L. Trilogy Laboratory Fluorometer

The Direct Calibration Procedure requires a calibration with one blank solution and at least one standard (single-point calibration) or up to five standard (multi-point calibration) solutions. The procedures outlined in the Trilogy Laboratory Fluorometer User's Manual, Version 1.1, August 01, 2003, P/N 998-7210

(www.turnerdesigns.com) will be followed.

ELEMENT B8: INSPECTION/ACCEPTANCE REQUIREMENTS for SUPPLIES and CONSUMABLES

Supplies and consumables will be purchased by the Laboratory Supervisor or the Project Coordinator. These persons are responsible for ordering the proper quality materials needed to support the project. The purchasing person will obtain the proper purchase order number from the Business Office and assure that the purchase is charged to the proper account.

The items ordered will be received by the Departments Mail Room and Laboratory personnel. The receiving person will inspect the material and check it against the packing slip. The packing slip will be turned in to the Business Office to allow payment.

All chemicals and reagents will be dated and inspected for proper expiration date.
Chemical standards used for calibration in the laboratory are purchased from reputable vendors with Certificates of Analysis listing the certified chemical content. Calibration materials such as thermometers and weights are traceable to National Institute for Standards and Technology (NIST) or American society of the International Association for Testing and Materials (ASTM).

Below is a list of the types of supplies and consumables used:

1. Field Supplies
   A. Water bottles, pH standards, meter maintenance supplies
   B. Metals bottles, filters, syringes, acid
   C. Pesticide bottles, vials, acid
   D. Bacteria reagents; media, dilution water, glassware; Petri dishes, filters, pipets, graduated cylinders.

2. Lab Supplies
   Parameter standards, chemicals for spikes, dilution bottles

3. Physical and Aggregate Properties
   A. Turbidity
      1. Reagents; turbidity free water, hydrazine sulfate, hexamethylenetetramine
      2. Glassware; pipets, volumetric flasks
   B. Total Dissolved Solids; Glassware; evaporating dishes
   C. Total Suspended Solids; Glass fiber filters

4. Metals
   A. Reagents; standards, acids, Matrix modifiers
   B. Glassware; volumetric flasks, pipets

C. Other supplies: pipet tips, pump tubes, test tubes, sample cups, graphite furnace tubes

5. Inorganic Nonmetalic Constituents
   A. Reagents; standards, color reagents.
   B. Glassware; volumetric flasks, pipets, beakers, flasks, distillation flasks
   C. Other supplies; sample cups, pump tubes, printer paper, chart paper, electrodes
6. Aggregate Organic Constituents
   A. Reagents; BOD buffers, acids, hexane
   B. Glassware; BOD bottles, flasks, volumetric flasks, pipets, condensers, sample tubes

7. Individual Organic Compounds
   A. Volatile Organics; Reagents: Standards, methanol
   B. Glassware; volumetric flasks, pipets, syringes
   C. Other Supplies; VOC vials

8. Pesticides and PCBs
   A. Reagents; standards, solvents
   B. Glassware; separatory funnels, volumetric flasks, pipets
   C. Other Supplies; sample vials, syringes

9. Extractable Base Neutrals/Acids:
   A. Reagents; standards and solvents
   B. Glassware; separatory funnels, volumetric flasks, pipets
   C. Other supplies; sample vials, syringes

ELEMENT B9: DATA ACQUISITION REQUIREMENTS (Non-Direct Measurements)

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

ELEMENT B10: DATA MANAGEMENT

Field Data

The data collected in the field is recorded in the field log book and on the chain of custody form. Upon receipt of the sample by the lab, the sample data, date, time, station number, is entered into the Laboratory Information Management System and issued a laboratory log number. The in-situ data (such as in stream water temperature, dissolved oxygen, pH, and flow severity) is entered into the system until it has been checked for quality assurance.

Laboratory Data

1. Manual Methods: Data generated by manual procedures (COD, Cyanide, O&G) are manually entered into the 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.

2. Automated Methods: Data generated by automated procedures, Auto Analyzer, Atomic Absorption, ICP, GCMS, etc. is directly transferred to the XLIMS . The data is usually processed after collection in a spreadsheet or edited to a usable form before transfer. All instrument generated paper is stored and kept for a minimum of seven years.

Control Mechanisms for Detection/Correcting Errors

The data is checked for errors at several points. The data must pass all precision and accuracy checks for both the field duplicates and the laboratory matrix spike replicates. The data must be with the allowed range, *ie* pH between 0 and 14. The data is manually checked for logical errors, *ie* dissolved fraction greater than the total. The test results for dissolved copper and/or zinc will be flagged if the results exceed the total recoverable results as set forth in the metals SOP.

Data is inspected by the analyst before uploading the results into the LIMS system, checking for QC failures leading to re-analysis of samples or sample dilutions. Once data is uploaded

into the LIMS system, the LIMS color codes any QC failures such as positive blanks, and the recovery of any QC samples which fall outside of acceptability limits. The lab manager reviews the data 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 will be initiated immediately. All lab data for that 'run' will be inspected to see if there are any trends or problems with multiple samples. If the error does not seem to have originated in the lab, the person who collected the sample will be contacted 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

1. The equipment used to handle the data consists of a Digital Equipment Co. VAX mainframe computer, Windows 2000 Cluster with RAID cabinet, several Pentium III and IV personal computers and the EPA supported STORET system.

2. The programs used to process compile and analyze the data include Water Quality Exchange (WQX), programs developed by ADEQ personnel or purchased programs such as Microsoft Office.

Data Storage

The data in the LIMS is stored on the computer disk in the laboratory, transferred to the ADEQ main computer and backed up daily. The data from all of the water quality monitoring networks is regularly transferred to EPA's WQX.

Data Use

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

ELEMENT C1: ASSESSMENT and RESPONSE ACTIONS

The Department QA Officer will conduct an annual inspection of the laboratory in order to review and assess analytical procedures, laboratory personnel, facilities, instrumentation, laboratory quality control and data handling. The QA Officer will also perform annual inspections of field duties to assess sampling methodologies, data handling, field quality control procedures and personnel.

Performance Testing Samples. The laboratory will participate in two performance testing studies annually provided by the U.S. Geological Survey and/or PT samples purchased from a TNI (The NELAC Institute) approved PT providers to supplement the USGS samples. These studies document the laboratory's proficiency and help compare our results with other laboratories throughout the country.

The Department QA Officer will conduct at least one field audit consisting of but not limited to sampling techniques, sample preservation, sample labeling, in-situ measurement techniques and field data handling techniques within the project period. A report on any deviations from the QAPP will be generated and distributed to the Project Officer, Laboratory Supervisor and Field Coordinator.

Corrective actions are taken when:

1. Quality control checks reveal a problem;
2. The QC data is out of control;
3. Deficiencies are cited during an audit; or
4. Data is determined to be questionable by an outlier test.

If for any of the above reasons precision and/or accuracy data falls outside the boundaries of the control 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 are re-analyzed.

ELEMENT C2: REPORTS TO MANAGEMENT

An annual summary quality assurance report should be prepared and submitted to the EPA Project Officer with the final report. The report will include precision and accuracy data, an evaluation of the completeness of data, and a discussion of any significant QA problems. The outline is below.

1. QA management (any changes)
2. Status of completion of the QA project plan
3. Measures of data quality from the project
4. Significant quality problems, quality accomplishments, and status of corrective actions
5. Results of QA performance audits
6. Assessment of data quality in terms of precision, accuracy, completeness, representativeness, and comparability
7. Quality Assurance related training
8. Department Quality Assurance Officer's report on field sampling techniques.

Semi-annual progress reports will be generated by the Project Officer and distributed to EPA, the ADEQ Water Division Chief, and Program Manager.

Annual field audit reports will be generated by the Department QA Officer. The report will outline the findings of the field QA audits and any corrective actions needed. The report will be distributed to the field personnel manager and the project manager.

An annual report outlining the results of performance testing, and data quality assessments will be prepared by the Project's Quality Assurance Officer and distributed to the project manager, field personnel manager and the lab manager.

ELEMENT D1: DATA REVIEW, VALIDATION, and VERIFICATION REQUIREMENTS

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

ELEMENT D2: VALIDATION and VERIFICATION METHODS

Data Verification

Verification refers to the process of confirming that a process or procedure was followed. Verification of data will be performed using self-assessments and by a technical review by the laboratory and project managers. The 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 Project Manager and the Chemist Supervisor 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.

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

The laboratory control checks are described in Element B5. These checks consist of the 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. There are two points for data checking:

1. After the initial data entry, a printout of the data stored in the computer is manually checked against the laboratory report forms.
2. The data is verified by a computer program which inspects the data for values out of the permissible or normal range.

Outliers

1. Quality Control Data
   A. Outliers from the laboratory quality control checks indicate sampling or analytical problems. All samples in these out-of-control situations will be re-analyzed or, if re-analysis is impossible; the data will be examined for any obvious causes.
   B. If reasons are found for the problem, eg. dilution error, 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.

C. If reasons for the problem are not found, the QC data will be tested to see if it is an outlier. The outlier test is found in Appendix 3. If the test results do not justify calling the suspect data point an outlier the data will be used in the QC database to calculate new control limits.

2. Sample Data
   A. When a value in a data set is suspiciously high or low it must be examined 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, eg. high flow, low flow, abnormal temperature, or any other explanation for the abnormal data.

   B. 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 outlier test in Appendix 3 should be used. The suspect data point and the 11 closest data points in the data set should be used in the test.

ELEMENT D3: RECONCILIATION WITH DATA QUALITY OBJECTIVES

The results obtained from the project will be evaluated at the midyear point in the project and at the end of the year. The completeness of the project will be reconciled with the expected outputs. The precision and accuracy of the data developed for the project will be reported to the decision makers to show the limits that should be placed on the data.

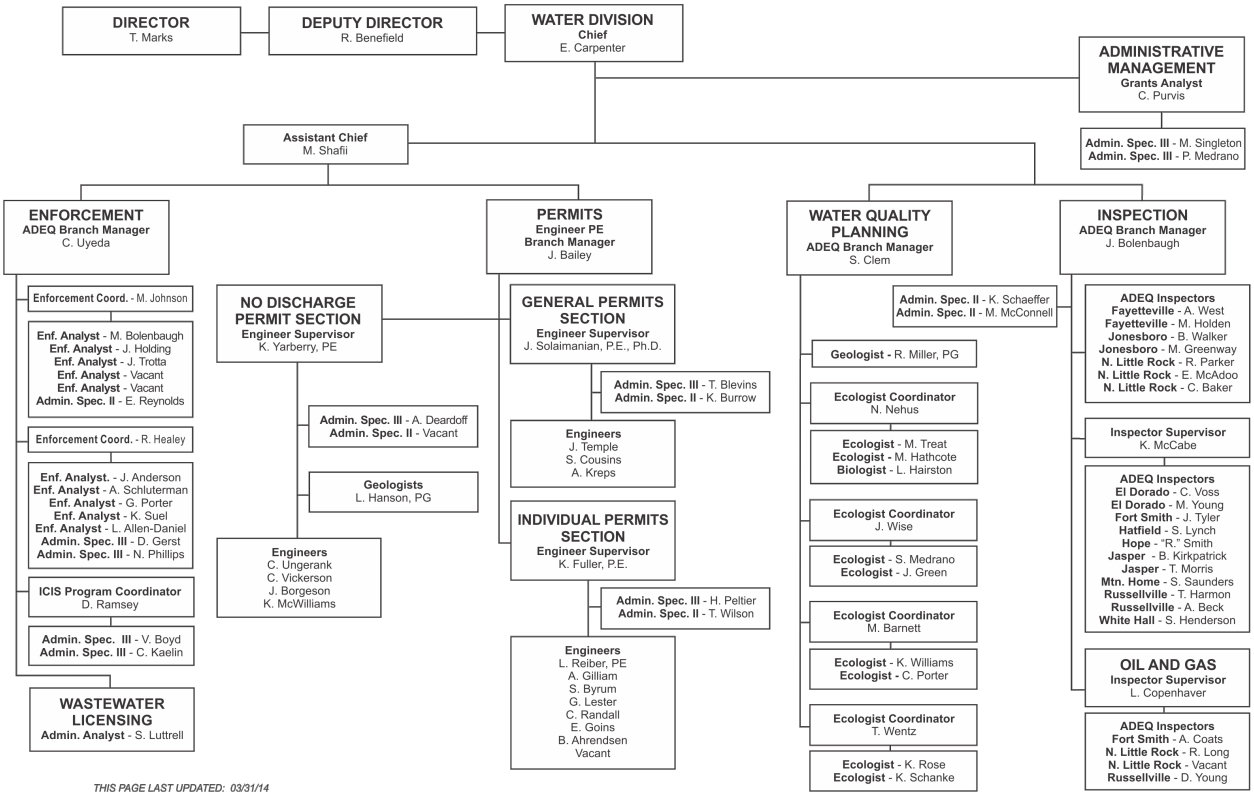
All data generated by this project that meets the QA/QC requirements set forth by this QAPP will be used to establish trend analyses; background or baseline levels of water quality parameters and indicate those areas of the State which may need a more intensive monitoring plan. Data produced from this survey will be compared with the water quality standards and criteria attainments and ecoregion (least-disturbed) reference steams established throughout the State.

APPENDIX 1: ORGANIZATIONAL CHARTS

The Organization Charts will be updated upon completion

ARKANSAS DEPARTMENT OF ENVIRONMENTAL QUALITY

Water Division Personnel Chart



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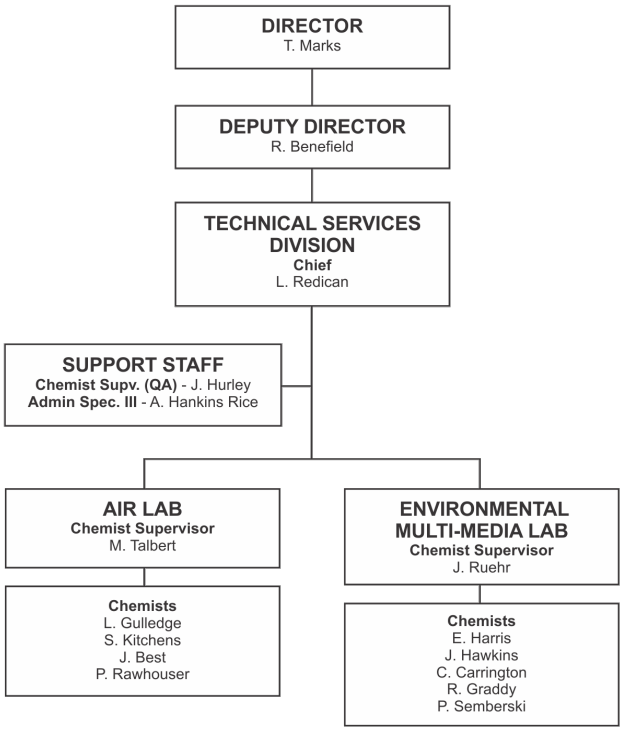
ARKANSAS DEPARTMENT OF ENVIRONMENTAL QUALITY

Technical Services Division Personnel Chart



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APPENDIX 2: QUALITY CONTROL LIMITS

The following limits are in effect for the period of July 1, 2016 to June 30, 2018

The field precision limits are used on field duplicate samples. They are based on the relative percent difference (RPD) of a set of duplicate samples.

The laboratory precision limits are based on the relative percent difference (RPD) of a pair of sample matrix spikes.

The laboratory accuracy limits are based on the percent recovery of the Laboratory Control Samples (LCS) spike.

The Lower Control Limits (LCL) and Upper Control Limits (UCL) are given in the table below. Please note some of the limits are method determined (signified by *) and others are default limits which may change when enough data points are in the LIMS to calculate historical limits.

Parameter	Field Precision RPD		Laboratory Precision RPD		Laboratory Accuracy % Recovery	
	LCL	UCL	LCL	UCL	LCL	UCL
pH	-10	10				
D.O.	-10	10				
Alkalinity	-20	20			90	110
Spec Cond	-10	10				
Turbidity	-20	20				
TSS	-20	20			90	110
TDS	-25	25			90	110
BOD	-20	20				
G&GA(BOD)			-25	25	84.6*	115*
COD	-20	20	-20	20	70	130
TOC	-20	20	-20	20	85	115
NH3-N	-20	20	-20	20	80	120
NO3-N	-20	20	-20	20	80	120
TKN	-25	25	-25	25	70	130
O-Phos	-20	20	-20	20	80	120
T-Phos	-25	25	-25	25	70	130
Cl	-25	25	-25	25	90*	110*
SO4	-25	25	-25	25	90*	110*
Br	-25	25	-25	25	90*	110*
F	-25	25	-25	25	90*	110*
FC-MF	-30	30				
CN	-20	20	-20	20	70	130

Parameter	Field Precision		Laboratory Precision RPD		Laboratory Accuracy % Recovery	
	LCL	UCL	LCL	UCL	LCL	UCL
Aluminum	20	20	20*	20*	85*	115*
Arsenic	20	20	20*	20*	85*	115*
Barium	20	20	20*	20*	85*	115*
Beryllium	20	20	20*	20*	85*	115*
Boron	20	20	20*	20*	85*	115*
Cadmium	20	20	20*	20*	85*	115*
Calcium	20	20	20*	20*	85*	115*
Chromium	20	20	20*	20*	85*	115*
Cobalt	20	20	20*	20*	85*	115*
Copper	20	20	20*	20*	85*	115*
Iron	20	20	20*	20*	85*	115*
Lead	20	20	20*	20*	85*	115*
Magnesium	20	20	20*	20*	85*	115*
Manganese	20	20	20*	20*	85*	115*
Mercury	20	20	20*	20*	85*	115*
Nickel	20	20	20*	20*	85*	115*
Potassium	20	20	20*	20*	85*	115*
Selenium	20	20	20*	20*	85*	115*
Sodium	20	20	20*	20*	85*	115*
Vanadium	20	20	20*	20*	85*	115*
Zinc	20	20	20*	20*	85*	115*
Herbicides	-50	50	-50	50	70	130
Pesticides	-50	50	-50	50	70	130
Semi-volatiles	-50	50	-50	50	70	130
Volatiles	-20	20	-20	20	70	130

MDLs and RDLs for Metals Analyses (ug/L)					
Constituent	MDL	RDL	Constituent	MDL	RDL
Aluminum	20.0	20.0	Lead	0.02	0.3
Arsenic	1.0	5.0	Magnesium	0.01	0.02
Barium	0.2	0.5	Manganese	0.07	0.3
Beryllium	0.4	2.0	Nickel	0.15	0.5
Boron	2.0	5.0	Potassium	0.01	0.02
Cadmium	0.05	0.1	Selenium	0.2	1.0
Calcium	0.03	0.03	Silver	0.02	0.05
Chromium	0.05	0.5	Sodium	0.01	0.2
Cobalt	0.05	0.5	Thallium	0.005	0.5
Copper	0.2	0.5	Vanadium	0.3	0.5
Iron	5.0	20.0	Zinc	0.3	1.0

APPENDIX 3: TEST FOR OUTLIERS
(Dixon Extreme Value Test, EPA/QA-G9/QA00)

Arrange the values in order of increasing value and calculate R using the following equation:

For sets of 3 to 7 values: $R = (X_N - X_{N-1}) / (X_N - X_1)$
For sets of 8 to 10 values: $R = (X_N - X_{N-1}) / (X_N - X_2)$
For sets of 11 to 13 values: $R = (X_N - X_{N-2}) / (X_N - X_2)$
For sets of 14 to 25 values: $R = (X_N - X_{N-2}) / (X_N - X_3)$

Where:

X_N = the suspect value
X_{N-1} = the value nearest the suspect value
X_{N-2} = the value second nearest the suspect value
X_1 = the value furthest from the suspect value
X_2 = the value second furthest from the suspect value
X_3 = the value third furthest from the suspect value

The calculated value for R is compared to the critical value in the table below. If the critical value is exceeded, the suspect value is considered to be an outlier and may be discarded. The level of significance for the critical value is 0.05.

Number of Values in Set	Critical Value for R	Number of Values in Set	Critical Value for R
3	0.941	14	0.546
4	0.765	15	0.525
5	0.642	16	0.507
6	0.560	17	0.490
7	0.507	18	0.475
		19	0.462
8	0.554		
9	0.512	20	0.450
10	0.477	21	0.440
		22	0.430
11	0.567	23	0.421
12	0.546	24	0.413
13	0.521	25	0.406

APPENDIX 4: FISH COMMUNITY BIOCRITERIA

Ozark Highlands Streams (> 10 mi^2 watershed)

METRIC	4	2	0
% Sensitive Individuals Avg. = 54.9 Std. = 15.1	>40	40-30	<30
% Cyprinidae (minnows) Avg. =57.6 Std. = 7.7	40-65	32-39 or 65-73	<32 or >73
% Ictaluridae (Catfishes) Avg. = 4.8 Std. = 2.5	>3[1]	1-3 [1]	<1 or >3 bullheads
% Centrarchidae (Sunfishes) Avg. = 5 Std. = 2.4	2-10[2]	<2 or 10-15[2]	>15 or >2 Green sunfish
% Percidae (darters) Avg. = 22 Std. = 7.6	>10	5-10	<5
% Primary Feeders Avg. = 32.7 Std. = 4.5	<37	37-42	>42
% ■Key• Individuals Avg. = 34.2 Std. = 7.9	>25	25-15	<15
Diversity Avg. = 3.23 Std. = 0.4	>2.83	2.83 - 2.43	>2.43

Total Score
25-32 Mostly Similar
24-17 Generally Similar
16-9 Somewhat Similar
0-8 Not Similar

[1] no more than 3% bullheads
[2] no more than 2% Green sunfish

Boston Mountain Streams (> 10 mi^2 watershed)

METRIC	4	2	0
% Sensitive Individuals Avg. = 43 Std. = 13	>30	30-16	<16
% Cyprinidae (minnows) Avg. = 43 Std. = 17	25-60	15-25 or 60-75	<15 or >75
% Ictaluridae (Catfishes) Avg. = 8.8 Std. = 7.3	>4[1]	2-4[1]	<2 or >1 bullheads
% Centrarchidae (Sunfishes) Avg. = 23.4 Std. = 14.8	10-40[2]	6-10 or 40-55[2]	<6 or >55 or >18 Green sunfish
% Percidae (darters) Avg. = 16.6 Std. = 4.8	>10	6-10	<6
% Primary Feeders Avg. = 24.3 Std. = 11.1	<35	35-45	>45
% ■Key• Individuals Avg. = 42.7 Std. = 6.7	>35	25-35	<25
Diversity Avg. = 3.45 Std. = 0.3	>3.15	3.15-2.85	<2.85

Total Score

25-32 Mostly Similar
24-17 Generally Similar
16-9 Somewhat Similar
0-8 Not Similar

[1]no more than 1% bullheads
[2]no more than 18% Green sunfish

Arkansas River Valley Streams (> 10 mi^2 watershed)

METRIC	4	2	0
% Sensitive Individuals Avg. = 12.8 Std. = 11.8	>3	1-3	<1
% Cyprinidae (minnows) Avg. = 35.3 Std. = 8.3	27-43	30-27 or 43-51	<20 or >51
% Ictaluridae (Catfishes) Avg. = 15.7 Std. = 10.4	>5[1]	3-5	<3 or >7 bullheads
% Centrarchidae (Sunfishes) Avg. = 21.0 Std. = 4.6	16-26[2]	11-16 or 26-31[2]	<11 or >31 or >12 Green sunfish
% Percidae (darters) Avg. = 11.9 Std. = 7.6	>4	1-4	<1
% Primary Feeders Avg. = 25.8 Std. = 5.9	<30	30-35	>35
% ▪Key• Individuals Avg. = 40.0 Std. = 19.0	>20	10-20	<10
Diversity Avg. = 3.74 Std. = 0.23	>3.51	3.51-3.28	<3.28

Total Score
25-32 Mostly Similar
24-17 Generally Similar
16-9 Somewhat Similar
0-8 Not Similar

[1]no more than 7% bullheads
[2]no more than 12% Green sunfish

Ouachita Mountains Streams (> 10 mi^2 watershed)

METRIC	4	2	0
% Sensitive Individuals Avg. = 33.8 Std. = 7.3	>24	16-24	<16
% Cyprinidae (minnows) Avg. = 51.7 Std. = 7.0	45-60	36-46 or 60-67	<36 or >67
% Ictaluridae (Catfishes) Avg. = 3.0 Std. = 1.7	>1[1]	<1 - 0.5	<0.5 or >2 bullheads
% Centrarchidae (Sunfishes) Avg. = 18.9 Std. = 7.1	8-26[2]	3-8 or 26-33[2]	<3 or >33 or >7 Green sunfish
% Percidae (darters) Avg. = 20.0 Std. = 5.4	>14	8-14	<8
% Primary Feeders Avg. = 37.3 Std. = 9.6	<48	48-58	>58
% ▪Key• Individuals Avg. = 36.0 Std. = 11.8	>23	10-23	<10
Diversity Avg. = 3.15 Std. = 0.52	>2.63	2.63-2.11	<2.11

Total Score
25-32 Mostly Similar
24-17 Generally Similar
16-9 Somewhat Similar
0-8 Not Similar

[1]no more than 2% bullheads
[2]no more than 7% Green sunfish

Gulf Coastal-Spring Influenced Streams (> 10 mi^2 watershed)

METRIC	4	2	0
% Sensitive Individuals Avg. = 18.4 Std. = 5.2	>3	2-3	<2
% Cyprinidae (minnows) Avg. = 31.5 Std. = 10.9	15-45	5-15 or 45-60	<5 or >60
% Ictaluridae (Catfishes) Avg. = 16.3 Std. = 8.3	>5[1]	2-5	<2 or >8 bullheads
% Centrarchidae (Sunfishes) Avg. = 19.0 Std. = 7.0	9-28[2]	4-9 or 28-38[2]	<4 or >38 or >8 Green sunfish
% Percidae (darters) Avg. = 8.0 Std. = 0.8	>6	3-6	<3
% Primary Feeders Avg. = 9.5 Std. = 9.0	<20	20-30	>30
% ▪Key• Individuals Avg. = 43.4 Std. = 12.2	>26	12-26	<12
Diversity Avg. = 3.89 Std. = 0.03	>3.79	3.79-3.69	<3.69

Total Score
25-32 Mostly Similar
24-17 Generally Similar
16-9 Somewhat Similar
0-8 Not Similar

[1]no more than 8% bullheads
[2]no more than 8% Green sunfish

Gulf Coastal-Typical Streams (> 10 mi^2 watershed)

METRIC	4	2	0
% Sensitive Individuals Avg. = 1.8 Std. = 1.4	>1	1-0.5	<0.5
% Cyprinidae (minnows) Avg. = 19.5 Std. = 13.0	5-35	<5 or 36-45	>45
% Ictaluridae (Catfishes) Avg. = 3.1 Std. = 2.9	>1[1]	0.5-1	<0.5 or >8 bullheads
% Centrarchidae (Sunfishes) Avg. = 32.3 Std. = 10.9	28-47[2]	18-27 or 48-57[2]	<18 or >57 or >8 Green sunfish
% Percidae (darters) Avg. = 14.5 Std. = 3.4	>10	6-10	<6
% Primary Feeders Avg. = 8.0 Std. = 6.5	<15	15-22	>22
% ■Key• Individuals Avg. = 22.4 Std. = 8.4	>19	13-19	<13
Diversity Avg. = 4.13 Std. = 0.24	>3.89	3.89-3.65	<3.65

Total Score
32-25 Mostly Similar
24-17 Generally Similar
16-9 Somewhat Similar
0-8 Not Similar

[1]no more than 8% bullheads
[2]no more than 8% Green sunfish

Delta-Least Disturbed Streams (> 10 mi^2 watershed)

METRIC	4	2	0
% Sensitive Individuals	N/A	N/A	N/A
% Cyprinidae (minnows) Avg. = 22.8 Std. = 19.9	10-40	5-10 or 40-55	<5 or >55
% Ictaluridae (Catfishes) Avg. = 9.2 Std. = 7.5	>3[1]	1-3	<1 or >13% bullheads
% Centrarchidae (Sunfishes) Avg. = 31.4 Std. = 16.5	20-45[2]	15-20 or 45-60[2]	<15 or >60 or >8% Green sunfish
% Percidae (darters) Avg. = 9.8 Std. = 6.3	>3	1-3	<1
% Primary Feeders Avg. = 6.5 Std. = 6.7	<15	15-25	>25
% ■Key• Individuals Avg. = 16.9 Std. = 14.9	>10	5-10	<5
Diversity Avg. = 3.73 Std. = 0.36	>3.37	3.37-3.01	<3.01

Total Score
22-28 Mostly Similar
21-15 Generally Similar
14-8 Somewhat Similar
0-7 Not Similar

[1]no more than 13% Bullheads
[2]no more than 8% Green sunfish

Delta-Channel Altered Streams

METRIC	4	2	0
% Sensitive Individuals	N/A	N/A	N/A
% Cyprinidae (minnows) Avg. = 18.8 Std. = 6.9	10-26	2-10 or 26-34	<2 or >34
% Ictaluridae (Catfishes) Avg. = 24.7 Std. = 15.2	6-40[1]	3-6 or 40-50[1]	<3 or >50 or >3 bullheads
% Centrarchidae (Sunfishes) Avg. = 23.6 Std. = 14.5	6-40[2]	3-6 or 40-55[2]	<3 or >55 or >30% Green sunfish
% Percidae (darters) Avg. = 0.1 Std. = 0.9	>0.1	0.1-0.05	<0.1
% Primary Feeders Avg. = 12.5 Std. = 8.1	<20	20-30	>30
% ■Key• Individuals Avg. = 47.5 Std. = 18.8	>25	10-25	<10
Diversity Avg. = 2.72 Std. = 0.21	>2.51	2.51-2.3	<2.30

Total Score
22-28 Mostly Similar
21-15 Generally Similar
14-8 Somewhat Similar
0-7 Not Similar

[1]no more than 3% bullheads
[2]no more than 30% Green sunfish

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