Quality Assurance Project Plan for

Water Quality Monitoring and Analysis of the Bennett Spring Watershed and Recharge Area

The Ozarks Environmental and Water Resources Institute (OEWRI)

Missouri State University

In support of the Southwest Missouri Council of Governments' Clean Water Act Section 604(b) grant entitled: Bennett Spring Branch Sub-Watershed: Planning for Wastewater Treatment and Water Quality Education G07-WQM-01

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PROJECT MANAGEMENT

Project and Task Organization

See Table 1 for personnel responsibilities, contact information and QAPP copy receipt. The organizational chart showing lines of authority and reporting responsibilities is shown in Figure 1.

Problem Definition and Background

Poorly functioning on-site wastewater systems have been perceived as a major contributor of nonpoint source pollution to Ozarks streams. Shallow soils, karst features, and lack of maintenance are often cited as reasons these systems fail in this region. Due to the importance of tourism to the local economy, many communities are concerned with protecting their water resources. Bennett Spring State Park is a major economic generator for Dallas and Laclede counties, and local community leaders are concerned about how on-site wastewater systems impact the water quality of Bennett Spring. The Bennett Spring Branch Watershed (43 sq. mi) is located in the Niangua River Basin (1,029 sq. mi) (Figure 2). Bennett Spring lies near the east edge of Dallas County with a recharge area that includes portions of Dallas and Laclede counties.

The Southwest Missouri Council of Governments (SMCOG) in cooperation with the Bennett Springs Area Water Protection Committee (BSWPC) has received a Clean Water Act 604(b) subgrant from the U.S. Environmental Protection Agency (EPA) Region 7, through the Missouri Department of Natural Resources (DNR), to address onsite wastewater issues in the watershed. The objectives of the subgrant are to:

- 1. Conduct a wastewater system feasibility study of the project area to determine the most cost-effective wastewater system that will meet the area's needs.
- 2. Create a plan to implement a wastewater district within, and under the authority of, the existing water district.
- 3. Provide for water quality education to enhance public awareness of the area's water quality issues and to build grassroots support for implementing a wastewater system that sustains the quality of the environment.
- 4. Provide for water quality assessment and monitoring in the project area to establish a baseline for determining water quality and future water quality needs and activities.

This QAPP represents the water quality monitoring component of the project. The specific goals of the water quality monitoring are:

- 1. Use the watershed approach and most up-to-date estimates of groundwater flow direction and recharge to determine water quality. Available historical water quality and groundwater data will also be used in the assessment.
- 2. Establish a baseflow sampling network and monitor 14 sites monthly for at least one year.
- 3. Interpret water quality trends and assess the spatial variability of water quality within the recharge area.

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During the 18 month period the water quality monitoring aspects will be addressed in this QAPP where the OEWRI will identify a baseline water quality trends and conduct an assessment of pollution sources (within the first six months). Monthly water monitoring will continue throughout the second year (month 7 through month 18). Once the monitoring is completed, the University, on behalf of the SMCOG, will submit a final water monitoring report. The yearlong water monitoring schedule will provide valuable data to analyze changes in water quality within the project area. In addition, the 14 newly identified water monitoring sites in and around Bennett Spring's 3-mile project area could be used in the future by Missouri Stream Teams, or other groups, to provide valuable long-term data and analysis. The Bennett Spring community leaders and its collaborating partners envision this project as a first step toward facilitating water quality protection activities and data gathering throughout the Niangua River Watershed.

PROJECT AND TASK DESCRIPTION

Project Schedule and Time Line

This project is organized into four phases. Phase 1 (November 2006 – February 2007) will include conducting a watershed assessment of establishment of sample sites and conducting a readiness assessment. Phase 2 (March 2007) will be establishing initial baseline water quality monitoring for nutrients, bacteria, temperature, dissolved oxygen, pH, conductivity, salinity, turbidity and velocity (to estimate discharge). Phase 3 (April 2007 – March 2008) will include the monthly monitoring of water chemistry and velocity along with a minimum of six nutrient sampling events and six bacteria sampling events occurring during baseflow conditions At 14 sites. Phase 4 will be preparing the final report. See Table 2 for project schedule and time line.

Work Schedule for Sample Collection and Analysis

Water chemistry parameters: temperature, dissolved oxygen, pH, conductivity, salinity, turbidity with velocity (to estimate discharge) will be monitored at the 14 sites described below once in phase 2 and monthly during phase 3 (for a total of 13 readings). Water chemistry parameters will be monitored using a Horiba U-22XD multiparameter probe. These data will be stored in the data logger associated with the instrument and downloaded in the office. Velocity measurements will be gathered using a Global Water FP201 Flow Meter and staff gage to estimate discharge at each site. Site specific data will be hand entered onto flow data record sheets provided and entered into a spread sheet in the office.

Water quality samples for nutrients (total phosphorus, total nitrogen) and bacteria (E. coli) will be collected at the 14 sites described below once during phase 2 and six times during phase 3. Surface water grab samples will be collected during baseflow using 500 mL bottles and immediately acidified to a pH <2 using sulfuric acid and stored on ice during the remainder of the trip. A 100 ml grab sample for bacteria will also be collected with a Whirl-Pak® Coli-test bag.

At the laboratory, the collected samples will be stored in refrigerators until they are analyzed by MSU laboratory assistants. Holding times will be strictly adhered to, to

avoid missed data. Analytical reports will be generated after the analyses. The reports are then reviewed by the analyst, the OEWRI QA officer and by the analyst's supervisor.

The data will be stored in Excel files dedicated to this project. These electronic files are stored on the computer server with controlled access (that is, access to these files will be limited to MSU personnel associated with this project). Paper copies of the analytical reports will be stored in the OEWRI office. MSU personnel shall submit raw data and analytical reports with any supporting information on the analysis to the project administer who will forward the information to the DNR project manager quarterly throughout the monitoring period.

Sampling Sites and Frequency

Sample sites have been established during Phase 1 (November 2006 – February 2007). Sample sites (14) have been determined based on water during low-flow periods (Figure 3). Due to the lack of access and absence of water during low-flow periods only 5 sites will be sampled within the Bennett Spring Branch Watershed. The remainder of the sites will be in the Bennett Spring recharge area (7) and upstream and downstream of the confluence of the Bennett Spring Branch and the Niangua River (2). Table 3 summarizes the sample sites selected for this project. Phase 2 (March 2007) will be establishing initial baseline water quality monitoring for nutrients, bacteria, temperature, dissolved oxygen, pH, conductivity, salinity, turbidity and velocity (to estimate discharge). Phase 3 (April 2007 – March 2008) will include the monthly monitoring of water chemistry and velocity along with a minimum of six nutrient sampling events and six bacteria sampling events occurring during baseflow conditions at the 14 sampling locations. Table 4 summarizes the sampling techniques for all analytes.

Target Water Quality Indicators

Field measured analytes:

1. Temperature (SOP: 1050R01 Horiba U-22): Water temperature is an important water quality parameter because it can affect the speed of chemical and biological reactions and the concentration of ions and gases. In karst areas, springs have lower temperatures than surface water runoff. Data will be collected using the Horiba U-22XD.

2. Conductivity (SOP: 1050R01 Horiba U-22): The first flush from surface water runoff in a rain storm carries concentrated analytes dissolved from surfaces, causing conductivity to be high. Data will be collected using the Horiba U-22XD.

3. pH (SOP: 1050R01 Horiba U-22): pH is a measure of the activity of hydrogen ions (H^*) in a solution and, therefore, its acidity or alkalinity. Low pH in rainfall can be a problem in some areas, however, due to the abundance of limestone in the region the Ozarks soil has a high buffering capacity and runoff pH generally remains around neutral, that is, pH of 7.0. Data will be collected using the Horiba U-22XD. If field

analysis of pH cannot occur, then the data will be listed as missing and a comment will be entered into the field notebook.

4. Turbidity (SOP: 1050R01 Horiba U-22): Turbidity is a measure of the clarity of water and can be caused by suspended materials, such as clay, silt, and organic matter. High turbidity may result from storm events. Data will be collected using the Horiba U-22XD

5. Dissolved Oxygen (SOP: 1050R01 Horiba U-22): The level of dissolved oxygen (D.O.) in water affects aquatic life, chemical activity, and pollutant behavior. Acceptable levels for Missouri streams are > 5 mg D.O. per L. for warm and cool water fisheries and >6 mg/L for Cold water fisheries.

6. Salinity (SOP: 1050R01 Horiba U-22): High salt concentrations are found in wastewater.

7. Global Water Flow Meter (SOP: 2060R01 Flow Meter): Velocity must be measured to estimate discharge at sample location to understand loads/yields.

Laboratory measured analytes:

1. Total Phosphorus (SOP: 3010R01 Total P): A spectrophotometer will be used to analyze for TP.

2. Total Nitrogen (SOP: 3020R01 Total N): Total nitrogen is a measure of organic nitrogen, ammonia, nitrite, and nitrate nitrogen. A spectrophotometer will be used to analyze for TN.

3. *Escherichia coli* (SOP: 4010R01 Ecoli IDEXX): The presence of *E. coli* in water samples is an indicator of fecal contamination. The IDEXX Quanti-Tray/2000 system is used to analyze samples for *E. coli* levels.

4. Total Coliform (SOP: 4010R01 Ecoli IDEXX): The presence of total coliform in water samples is an indicator of fecal contamination. The IDEXX Quanti-Tray/2000 system is used to analyze samples for total coliform levels.

Quality Objectives and Criteria for Measurement Data

The objective of this project is to establish a baseline data for the Bennett Springs Recharge Area during baseflow conditions that will indicate water quality of the shallow aquifer providing flow to the spring and stream. These data will be used to compare sites to assess the spatial variability of water quality within the recharge area. All field and laboratory analytical data are evaluated based on established measurement performance criteria as listed in Table 5.

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Data Quality Indicators, Definitions

<u>Accuracy</u>: a measure of the overall agreement of a measurement to a known value; includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations. Accuracy will be measured by analyzing a reference material and spiked matrix samples (see Table 5).

<u>Bias</u>: a consistent deviation of measured values from the true value, caused by systematic errors in a procedure. Bias will be measured by analyzing reference materials and spiked matrix samples (see Table 5).

<u>Comparability</u>: the measure of confidence that one data set can be compared to another and can be combined, if applicable, for the decisions to be made. Water samples are collected and analyzed according to the standard operating procedures used at Missouri State University and OEWRI for all water quality projects.

<u>Completeness</u>: a measure of the amount of data needed to be obtained from a measurement system. It is expected that all samples will be collected and analyzed. However, it is known that lost samples and missed analyses can occur.

<u>Precision</u>: a measure of the degree of agreement among replicate analyses of a sample. For this project, samples will be collected in duplicate (field duplicates) and single samples will be analyzed in duplicate in the laboratory (laboratory duplicates) (see Table 4).

<u>Representativeness</u>: the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. For the goals of this study, these samples will be considered representative of the conditions found at the collection sites and within the Bennett Spring Branch Sub-Watershed/Niangua River Watershed

<u>Sensitivity</u>: the capability of a method or instrument to discriminate between measurement responses representing different level of the variable of interest. This is also known as the detection limit. For this project the method detection limit (MDL) is determined (see Table 4)

Special Training and Certification

All personnel who collect and analyze samples for this project will receive appropriate training for all methods needed to complete the study following the necessary SOPs. Records of this training will be kept with other documents related to this project. The final storage location for these records will be the OEWRI office (currently room 328 Temple Hall).

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Documents and Records

The documents and records produced for this project will be stored in the OEWRI office in a file entitled: "Water Quality Monitoring and Analysis of the Bennett Spring Watershed and Recharge Area". The documents listed below will be included in this file. Electronic copies of all reports, plans and procedures will be issued to all individuals on the distribution list, unless otherwise requested. A paper copy of each document will be kept on file in the OEWRI office.

Documents and records will be retained for a minimum of five years. After that time the documents will be reviewed and a decision to retain the records for a longer period will be made. Electronic records are retained on the server at MSU. There is in place a system to automatically backup all data files.

<u>Quality Assurance Project Plan (QAPP)</u>: This document will be updated as needed by the QA manager. The DNR project manager, through the project administer, must then approve any updates prior to those changes being distributed. Updates may require that the document be reprinted and distributed to those listed in Table 1. If the changes do not alter the plan the QA manager may use e-mail to notify the personnel on the distribution list of the changes.

<u>Standard Operating Procedures (SOPs)</u>: Analytical, collection, and other procedures are documented in individual SOPs. These documents are prepared, edited, and updated by the QA manager. Project personnel are required to review all SOPs that pertain to their functions and responsibilities. Outdated SOPs are archived in the OEWRI office in both a paper and electronic versions. SOPs used for this project are attached in Appendix B.

<u>Chain of Custody forms</u>: Chain of custody / sample collection forms are completed for each sample collection run. These forms are stored with the project data in the OEWRI office.

<u>Field Notebooks</u>: Field notebooks will be completed for this project. Any data related to this project will be recorded within the book. The field personnel will keep appropriate records of field events and include such items as sites visited, time of arrival, samples collected, weather conditions, etc. The analyst should sign or initial for each date that the notebook is used. These notebooks will be archived with the project records in the OEWRI office.

<u>Laboratory Bench sheets</u>: These forms are generated with each analysis. They may include forms, computer printouts, or other records of analytical procedures. Sample and quality control data will be included on these forms. These are stored with the project data.

<u>Quality Assurance documents</u>: Any document that describes QA processes in the field or laboratory and related to this project will be stored in the OEWRI office with other

records for this project. Some records are continuous, for example, instrument maintenance data, and remain with the instrument in log books that are attached to that instrument.

<u>Final and Quarterly Progress reports</u>: A copy of all progress, quarterly and final reports will be kept in the OEWRI office. These reports may also include presentations given at conferences; copies or the original will be stored in the OEWRI office. The DNR project manager must review all reports, presentations, media releases, etc. prior to publication or distribution. These items must be sent to the project administer who will forward the information to the DNR project manager.

DATA GENERATION AND ACQUISITION

Sampling Process Design

The objective of this project is to establish a baseline data for the Bennett Springs Recharge Area during base flow conditions that will indicate water quality of the shallow aquifer providing flow to the spring and stream. These data will be used to compare sites to assess the spatial variability of water quality within the recharge area. The 14 sample sites were chosen based on:

- 1. Road access
- 2. Proximity to known dye-trace locations
- 3. Distributed throughout the recharge area
- 4. Having permanent year round flow

Sampling Methods

Surface water samples for bacteriology analyses are collected by the grab sampling technique (SOP: 4010R01 Ecoli IDEXX.doc) from flowing water. The 100 mL Coli-Test bags are either dipped into the stream by hand or at the end of a sampling pole. Duplicate samples will be taken every tenth sample. Care should be taken to not skim the surface while collecting samples. The bacteriology Coli-Test bags are purchased and will be discarded after use. These bags are sterilized by the manufacturer.

Surface water samples for nutrient analysis are collected by the grab sampling technique (SOP: 1040R01 Water Sampling) using 500 mL plastic bottles from flowing water. Duplicate samples will be taken every tenth sample.

A Horiba U-22XD multi-parameter water quality testing system (SOP: 1050R01 Horiba U-22) will be used to collect temperature, pH, turbidity, D.O., salinity and conductivity data in the field. Duplicate readings will be taken every tenth sample.

Discharge will be estimated using the Global Water FP201 Flow Meter (SOP: 2060R01 Flow Meter) from mean velocity and a stage gage to measure water depth at the sample site.

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Sample Handling and Custody

See Table 6 for sample handling conditions for each analyte of interest for this project.

Field measurements of velocity and stage will be recorded on the flow record sheet provided in the SOP to estimate discharge. Data collected and stored on the Horiba's data-logger will remain in the custody of the field personnel until return to the laboratory or office. At the laboratory or office the data will be downloaded to computer program files.

Water samples are collected in appropriate bottles or bags for each parameter. A label will be affixed to each container (see below for example) and will contain the following information: date and time of collection, site code, project, list of analytes, and sample collector's initials (see SOP: 1040R01 Water Sampling for procedures for completing the bottle label). After collection, the proper preservative is added to the bottle, the bottles are placed into a cooler containing ice, and the samples are transported to the laboratory.

Date:	Time:	
Site:	Project:	
Analyze for:		
Collected by:		
Missouri State University		
Ozarks Environmental and Wate	er Resources Institute	
Examp	ole of bottle label.	

A Sample Collection form (see SOP: "1030R01 Chain of Custody.doc") will be completed for each set of samples. The chain of custody section of the sample collection form will be completed as the samples are transferred at the laboratory following the instructions outlined in the SOP (1030R01 Chain of Custody).

Sample bottles that are not used for immediate analysis will be stored in the laboratory refrigerator. Upon completion of the analyses, including review of data, the sample may be discarded. Re-analysis can occur if sample remains in the bottle and the holding time has not been exceeded. At no time will a re-analysis take place on samples when the holding time has expired.

Analytical Methods

See Table 4 for a list of analytes, SOPs, and method performance criteria. Analyses are completed as soon as possible after collection and within the allowable holding times. Samples are not disposed of until after the analyses are complete and data has been reviewed. If a sample is analyzed after the holding time has expired a comment will be recorded on the data analysis bench sheet.

When problems arise with the analytical method, for example, blanks exceeding the detection limit, the procedures will be reviewed by the analyst and the laboratory supervisor and/or the Project QA Manager. Corrections will be made and samples reanalyzed if possible. The problem will be documented in the instrument log book.

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Quality Control

Quality control is the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer. This system of activities and checks is used to ensure that the measurement systems are maintained within prescribed limits, provide protection against unforeseen conditions and ensure the results are of acceptable quality.

The quality control checks used in this project are listed in Table 4. Duplicate samples, field and lab, will be used as a check for precision. Matrix spike samples and reference samples (LFM and LFB in Table 4, respectively) are used to measure bias and accuracy. Sensitivity is determined by analyzing equipment, method and reagent blanks.

One spiked sample will be analyzed for every 20 samples analyzed. Reference samples and laboratory duplicates will be analyzed at a frequency of one per 10 samples analyzed. One field duplicate will be collected for every ten samples collected.

Quality control data outside the acceptance limits or exhibiting a trend are evidence of unacceptable error in the analytical process. Corrective action will be taken as soon as possible to determine and eliminate the source of the error. Corrective actions begin with the analyst, who is responsible for knowing when the analytical process is out of control (Standard Methods, 2005). See Table 6 for error types and corrective action measures. All corrective actions taken will be recorded in the instrument log book to be used as a reference to avoid repeating the same error.

If a sample batch is reanalyzed because a QC sample was out of control, the second set of results will be reported (if all QC are within control limits) for the project. However, a comment will be written on the data sheet that the data is a reanalysis and the reason for the reanalysis will be recorded. The initial analysis data sheet will be retained for the QC file associated with the project. All QC data, in and out of control, will be recorded on the control charts.

Instrument and Equipment Testing, Inspection, and Maintenance

Field and laboratory equipment and instruments will be maintained to prevent down time and missed sample data. See Table 7 for a list of instrumentation and equipment and the approximate schedule for preventive maintenance. Preventive maintenance procedures are also listed in some SOPs. Preventive maintenance activities will be recorded in the log book associated with the instrument. After a corrective activity has been completed, the instrument will be tested to ensure that it functions appropriately for the analysis in question.

For routine maintenance procedures an adequate supply of spare parts will be kept on hand. When parts are used up, new ones will be purchased before they are needed. If there is a major instrument break down the manufacturer may be contacted to perform a service call for repairs.

Instrument and Equipment Calibration and Frequency

Laboratory and field analytical instrumentation require calibration to ensure quality data. Calibration procedures follow the instrument manufacturer's recommendations.

Initial calibrations of field and laboratory instruments will be performed before each batch of samples. If linear regression is used to fit the calibration curve, then the minimum correlation coefficient value should be 0.995. To determine if calibration points are acceptable, compare each point to the curve and recalculate. An acceptable point will result in a calculated value of the expected value \pm 10% (Standard Methods, 2005).

Calibration verification will be done by analyzing a calibration standard periodically to ensure that the instrument performance has not changed. Analysis of the verification standard will be after every 10 samples during the analytical run. A verification standard will be acceptable if its value is within $\pm 10\%$ of the expected value.

See Table 8 for a list of instruments that require calibration. The type of calibration is listed in the table and a detailed description of the calibration procedure is included in the respective SOPs for the analyte in question.

Inspection and Acceptance of Supplies and Consumables

Adequate quantities of supplies and consumables are inventoried for this project. When the number of items needed begins to run low, replacements are ordered from the vendor. Chemicals are ordered as needed for laboratory analyses. Reference standards for calibrating instruments are received with "certificates of analysis" documents from the supplier.

The IDEXX system for the *E. coli* analysis requires the use of Quanti-Tray/2000. These are purchased from IDEXX Laboratories. New batches of the Quanti-Trays are tested with positive and negative control test organisms. The acceptable result for these tests is the correct identification and enumeration of the test organisms.

Other supplies, for example, bottles, filter paper, and pH test strips, are not tested prior to use. Analysts will employ good laboratory practices and observe all processes for changes that may be caused by a new batch of supply items. If a process does appear to be affected by a supply item, a corrective action response will be initiated. This may require discontinuing the use of that item and ordering replacement items.

Non-direct Measurements

There are no non-direct measurements required for this project. However, the project assistant may want to obtain weather data from the National Weather Service to check rain totals.

Data Management

Data are generated in many steps from sample collection to laboratory analyses, calculations and observations. All data are recorded on laboratory bench sheets, field

notebooks, in instrument data loggers or on instrument software. Following are the procedures that will be followed for managing data for each type of data collection.

<u>Field notebooks</u>: The field notebook will be similar to item number 8152-55 manufactured by Sokkia. This book has water resistant surfaced pages. Notes are written in indelible ink. Personnel will record all field observations in this book at the time of their visit. The date, time, sites visited, samples taken, other personnel present, weather conditions, and other information deemed necessary and appropriate will be recorded. The analyst should initial or sign each page. The notebook will be dedicated to this project. When the book is filled or the project completed, the notebook will be stored in the OEWRI office.

Laboratory bench sheets: Bench sheets will be completed for every analysis. Methods that require bench sheets have the sheets available as attachments within the SOP. The analyst should record all information on the forms using indelible ink. QC calculations, for example, spike percent recovery, will be recorded on the form in the "Comments" section of the bench sheet. Errors are crossed out with a single line, the correct entry is made and the analyst initials the correction. Completed data are transcribed into an Excel spreadsheet for further use. Completed bench sheets are stored with the project file in the OEWRI office.

<u>Field Instrumentation</u>: Data internally on the Horiba's data-logger are brought back to the office or laboratory where the data will be downloaded to a computer file. A print out of the data will be generated which will be used for data review. Other than transferring the data to an Excel file, there is no way to save the raw instrument data for future use. When the data logger is full (from this and other projects) the data is purged from the instrument. The completed and reviewed data printouts will be stored in the project file in the OEWRI office.

Data records will be stored for a minimum of five years after the completion of the project. After five years the data will be reviewed to determine if any part of the data may be discarded. The decision to retain archived data will be made by the OEWRI director and QA manager.

ASSESSMENT AND OVERSIGHT

Assessments and Response Actions

The Project's activities will be assessed to identify and correct any potential or existing problems before the data is affected. A readiness review will be conducted prior to starting the project. Proficiency test samples will be procured for assessing analytical skill. A surveillance assessment will be conducted throughout the project. Each of these assessments is discussed below. Handling of the results for these assessments is discussed in the next section.

<u>Readiness Review</u>: Prior to the initiation of sampling, the QA Manager will review with the project Graduate Assistant all aspects of sampling and analyses. Items that will be covered in this assessment are; location and preparation of sample bottles, use of chain of custody forms, analytical processes including necessary quality control analyses, sample site locations including site codes, the use of field instrumentation and sampling devices, and how to handle data after it is generated.

<u>Proficiency Testing</u>: A known-concentration sample will be purchased from an appropriate vendor, such as, the USGS (<u>http://bqs.usgs.gov/srs/</u>) or Environmental Resource Associates (http://www.eraqc.com). The sample will be assigned to the analyst without informing the analyst of the sample's source. The sample will be treated the same as other samples. The results will be submitted to the supplier for evaluation, or if the QA manager knows the correct concentration, the analyst's results can be "graded" upon completion.

<u>Surveillance Assessment</u>: Surveillance is the observation of ongoing work to document conformance with specified requirements and/or procedures, such as those given in the QAPP or in SOPs. These observations will be continuous throughout the project and will be conducted by the QA manager and the co-principal investigators. Any deficiencies or problems detected will be addressed as soon as possible. Surveillance and review will continue to ensure that corrections have been implemented for all future uses. Documentation may include hand written notes, copies of e-mail, or other forms that will be stored in the project file. These documents may be useful for future projects.

Reports to Management

A monitoring technical report containing statistical evaluations of all water quality and discharge data collected in the study will be prepared at the end of the second year. This report will include objectives, methodology, results, interpretations, tables, graphs, pictures and maps. A final report will be developed and submitted. Brief summary reports of the assessment findings, discussed above, will be prepared by the QA officer. These may be issued as e-mail messages or as a Word file in an e-mail attachment. Reports will be generated after each nutrient and bacteria sampling in Phase 3. Copies of all reports will be stored in the project file in the OEWRI office and sent to the project administer who will forward the information to the DNR project manager.

DATA VALIDATION AND USABILITY

Data Review, Verification and Validation

These procedures are summarized as follows: data are reviewed for completeness and correct calculations, data are verified against quality control parameters, and data are validated against project goals and objectives. <u>Data Review</u>: Sample collection forms, field instrument data printouts, laboratory bench sheets, and other sources of project data will be reviewed for transcription, calculation, reduction, and transformation errors. Data review is also a completeness check to determine if there are any deficiencies such as missing or lost data. Errors will be corrected when found. Missing data will be noted in the project narrative of the final report. The project analysts, OEWRI Quality Assurance officer, and faculty advisors will review all data.

<u>Data Verification</u>: Data verification is the evaluation of the data collected for the project compared to the requirements outlined in this QAPP, the original project agreement, and SOPs. Analytical data are compared to required levels of precision and accuracy as outline in the analyte's SOP. If the levels are not met, then a cause for the discrepancy will be determined. The result of this determination will be whether the data may be used with qualifications or not used. After the verification process it may be possible to recollect or reanalyze. The analyst, QA officer, faculty, and principal investigators are all responsible for data verification during the project.

<u>Data Validation</u>: One goal of data validation is to evaluate whether the data quality goals established during the planning phase have been achieved. Using the reviewed and verified data, the validation process compares the results with the objectives of the project stated in the Problem Definition and Background section.

Verification and Validation Methods

The verification method includes checking all bench sheets, data forms, and records for complete and accurate transcription of data, correct calculations, and appropriate comparison of quality control data to established limits. The reviewer will indicate on any form verified that this process has occurred. Any deviations from expected values will be noted on the report forms. Corrections can be made by crossing out the incorrect value with a single line, writing in the correct value, and initialing the correction.

The validation method involves reviewing the data and reports and comparing that information to what was expected as outlined in this document. Deviations from what is required will be noted and a comment will be added to the final report indicating whether, or how, the deficiency will affect the final interpretations.

Reconciliation with User Requirements

The goal of this project is to establish baseline data for baseflow conditions for the Bennett Springs Recharge Area. These goals will be met by the data generated following the procedures outlined in this and related documents, for example SOPs. The final report will include descriptions of water quality runoff results found at each site. Spatial and temporal trends will be identified where seen. Recommendations will be made for future studies based on pollutant concentrations and runoff amounts.

TABLESTable 1. Personnel, Responsibilities and QAPP Receipt.

Name and Title	Organization	Responsibilities	Contact Information	QAPP Receipt/ Control number
Dr. Robert T. Pavlowsky Director, Principal Investigator	Missouri State University, OEWRI	Overall supervision of entire project. Review data. Assign tasks. Procure funding	417-836-8473 BobPavlowsky@MissouriState.edu	1
Heather Hoggard Project Supervisor/ QA/QC Manager	OEWRI	Project coordination and oversight. QA/QC regarding laboratory procedures.	417-836-3198 hhoggard@MissouriState.edu	2
Dr. Jack Steiert, MSU Faculty	MSU Biology	Supervise bacteria analyses	417-836-6916 JohnSteiert@MissouriState.edu	3
Dr. Richard Biagioni, MSU Faculty	MSU Chemistry	Supervise chemistry analyses	417-836-4649 <u>RNBiagioni@MissouriState.edu</u>	4
Ms. Stacia Bax, Project Manager	Missouri DNR	DNR Project Manager	573-526-1386 stacia.bax@dnr.mo.gov	5
Mr. John Madras, Division Quality Control Officer	Missouri DNR	DNR Quality Assurance	573-522-9911 john.madras@dnr.mo.gov	6
Ms. Trish Rielly, QAPP Manager	Missouri DNR	DNR QAPP Manager	573-526-5297 trish.rielly@dnr.mo.gov	7
Dr. William A. Alter III	MSU	Office of Sponsored Research and Programs	417-836-5972 WilliamAlter@MissouriState.edu	8

Activity	Date (MM/DD/YYYY)			Deliverable Due Date	
	Anticipated Start Date	Anticipated Completion Date	Deliverable		
Phase 1. Select sampling sites	11/01/2006	12/15/2006	Approved sample site map	12/15/2006	
Phase 1. Readiness Assessment	12/18/2006	12/31/2006	Memo	12/31/2006	
Phase 2. Baseline Sampling	01/01/2007	03/31/2007	Memo	03/31/2007	
Phase 3. Monthly Water Chemistry Sampling	04/01/2007	03/31/2008	Memo	03/31/2008	
Phase 3. Nutrient/Bacteria Sampling	04/01/2007	03/31/2008	Memo	03/31/2008	
Phase 4. Final Report	04/01/2008	06/30/2008	Report	06/30/2008	

Table 2. Project Schedule Time Line.

Table 3. Sample Site Summary

Site ID	Easting	Northing	Stream Name	Site Description	Site Location
1	507231.319842	4144309.142760	E. Fork Niangua	Recharge Area	Blackhorse Rd. Bridge east of State Hwy Y
2	506740.017227	4144834.094600	Niangua R.	Recharge Area	State Hwy Y Bridge 2.5 miles east of State Hwy W
3	512673.966756	4153137.538590	Jones Creek	Recharge Area	State Hwy B Bridge 1 mile north of State Hwy M
4	509441.216000	4158426.473670	Dousinbury Creek	Recharge Area	State Hwy B Bridge 4.5 miles north of Site 3
5	506783.801874	4162462.890700	Fourmile Creek	Recharge Area	Pisgah Rd. Bridge 0.25 mile south of State Hwy 32
6	519122.849915	4164910.435990	Bennett Spring Br.	Watershed	State Hwy 32 bridge 3 miles east of State Hwy OO
7	516294.382420	4167608.358840	Bennett Spring Br.	Watershed	Memphis Rd. Bridge 2 miles east of State Hwy OO
8	510430.751728	4172764.872650	Niangua R.	Receiving Water	Moon Valley Rd. Bridge 1 mile west of State Hwy OO
9	512728.346510	4174241.018770	Bennett Spring Br.	Watershed	Above Bennett Spring in State Park
10	512536.764285	4174501.023220	Bennett Spring	Spring	At Bennett Spring in State Park
11	512727.133202	4175177.488080	Bennett Spring Br.	Watershed	Below Bennett Spring in State Park
12	512291.919602	4176760.924800	Niangua R.	Receiving Water	Downstream of State Hwy 64 Bridge at MDC Access
13	527115.224827	4168168.526400	Unnamed Trib of the Dry Auglaize Creek	Recharge Area	State Hwy 32 Bridge 1.5 miles west of US Hwy 66
14	528970.800405	4155152.838920	Brush Creek	Recharge Area	State Hwy PP Bridge 0.5 miles south of State Hwy C

Coordinate system = UTM NAD83 Zone 15

Recharge Area = Bennett Spring recharge area Receiving Water = Stream receiving water from Bennett Spring Branch Spring = Outflow of the Bennett Spring

Watershed = Topographic drainage area of Bennett Spring Branch watershed

Table 4. Sampling Techniques

Sampling Device or Procedure	Collected By	Sites	Location	Number collected	Analytes
Manual Grab Sample	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 6	Nutrients
Manual Grab Sample	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 6	Bacteria
In situ	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 12	Temperature
In situ	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 12	рН
In situ	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 12	Conductivity
In situ	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 12	D.O.
In situ	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 12	Salinity
In situ	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 12	Turbidity
In situ	Project Assistant	all	Stream	Phase 2 = 1 Phase 3 = 12	Velocity

 Table 5. Measurement Performance Criteria.

Matrix = Water	Sampling Procedure	= Grab Sample		
Parameter	SOP	Data Quality Indicator	Measurement Performance Criteria	QC Sample Type to assess Measurement Performance
Conductivity	1050R01 Horiba U-22	Accuracy	± 20%	LFB, LFM
		Bias	NA	ND
		Precision	± 20% RPD	FD, LD
		Sensitivity	0 mS/m	LRB
Dissolved Oxygen	1050R01 Horiba U-22	Accuracy	± 20%	LFB, LFM
		Bias	NA	ND
		Precision	± 20% RPD	FD, LD
		Sensitivity	0 mS/m	LRB
Escherichia coli	6010R01 Ecoli IDEXX	Accuracy	NA	ND
		Bias	NA	ND
		Precision	± 20% RPD	FD, LD
		Sensitivity	1 MPN/100mL	LRB
рН	1050R01 Horiba U-22	Accuracy	± 20%	Reference standard
		Bias	± 20%	Reference standard
		Precision	± 20% RPD	LD, FD
		Sensitivity	1 unit	NA
Salinity	1050R01 Horiba U-22	Accuracy	± 20%	Reference standard
		Bias	± 20%	Reference standard
		Precision	± 20% RPD	LD, FD

Matrix = Water	Sampling Procedure :	= Grab Sample		
Parameter	SOP	Data Quality Indicator	Measurement Performance Criteria	QC Sample Type to assess Measurement Performance
		Sensitivity	1 unit	NA
Temperature	1050R01 Horiba U-22	Accuracy	NA	ND
		Bias	NA	ND
		Precision	± 20% RPD	FD, LD
		Sensitivity	0° C	Ice bath
Total Nitrogen	3020R01 TotalN	Accuracy	± 20%	LFB, LFM
		Bias	± 20%	LFB, LFM
		Precision	± 20% RPD	LD
		Sensitivity	≤ 0.05 mgN/L	MDL, LRB
Total Phosphorus	3010R01 TotalP	Accuracy	± 20%	LFB, LFM
		Bias	± 20%	LFB, LFM
		Precision	± 20% RPD	LD
		Sensitivity	≤ 0.005 mgP/L	MDL, LRB
Turbidity	1050R01 Horiba U-22	Accuracy	± 20%	LFB
		Bias	± 20%	LFB
		Precision	± 20% RPD	LD, FD
		Sensitivity	1 NTU	LRB

*LFB = Laboratory Fortified Blank (reference sample), LFM = Laboratory Fortified Matrix (spiked sample)

LD = Laboratory Duplicate, FD = Field Duplicate, LRB = Laboratory Reagent Blank, MDL = Method Detection Limit ND = Not Determined, NA = Not Applicable, RPD = Relative Percent Difference

Table of Gample Conce					
Analyte	Bottle Type	Bottle Size	Preservative	Holding time	SOP Reference
Total Nitrogen	Plastic	500-mL	H_2SO_4 to pH ≤ 2 lce	28 days	3020R01 TotalN
Total Phosphorus	Plastic	500-mL	H_2SO_4 to pH ≤ 2 lce	28 days	3010R01 TotalP
E. coli	Plastic bag	100-mL	Ice	3 hours	4010R01 Ecoli IDEXX
Field Parameters	These parame	eters are collected	d <i>in situ</i> .		
Temperature	none	none	none	none	3060R01 Temperature
Turbidity	none	none	none	none	1050R01 Horiba U-22
рН	none	none	none	none	1050R01 Horiba U-22
Conductivity	none	none	none	none	1050R01 Horiba U-22
Dissolved Oxygen	none	none	none	none	1050R01 Horiba U-22
Salinity	none	none	none	none	1050R01 Horiba U-22
Velocity	none	none	none	none	2060R01 Flow Meter
Discharge	none	none	none	none	2050R01 Flow Discharge

Table 6. Sample Collection Conditions for Analytes.

QC Type and Error	Corrective Action	Comment*			
Laboratory Reagent Blank > MDL	 Analyze another blank; if 2nd LRB is acceptable, then data is acceptable. If 2nd LRB fails, then re-prepare and re- analyze affected samples 	These data are associated with an LRB result that is > the MDL for this analyte.			
Spiked samples (LFM) fails	 If Reference sample (LFB) is acceptable, then qualify the data If LFM and LFB fail, then re-prepare and reanalyze the affected samples. 	These data are associated with a LFM recovery result that is > UCL (or < LCL).			
Reference sample (LFB) fails	 Analyze another LFB. If 2nd LFB fails then check another source for the reference material. If the 2nd source is acceptable, then re- prepare and reanalyze affected samples. 	These data are associated with a LFB recovery result that is > UCL (or < LCL).			
Calculations	 Check calculations for error, correct if found 	No comment needed for corrected calculations.			
Calibration Standards fail	 Check calibration standards against the reference sample. If calibration standards fail then re- prepare and reanalyze the calibration standards and affected samples. 	No comment needed for reanalyzed calibration standards.			
*If the QC sample fails and the samples cannot be reanalyzed, then record the comment on the data sheet.					
UCL = Upper Control Limit, LCL = Lo	wer Control Limit				

Table 7. Quality Control Corrective Action Plan. (Standard Methods, 2005)

Equipment / Instrument	Maintenance, Testing, or Inspection Activity	Frequency	SOP Reference
Sampling Equipment			
Horiba U-22XD	Auto Calibration	Before each use	1050R01 Horiba U-22
	Cleaning	After each use	
	Manual Calibration	Monthly	
	Battery replacement	Monthly	
	Rebuild DO Sensor, Recharge pH Probe	Bi-Monthly	
Laboratory Equipme	ent		
Spectrophotometer	Create calibration curve	For each use	3010R01 Total P
Spectrophotometer	Create calibration curve	For each use	3020R01 Total N

Table 8. Maintenance, Testing, and Inspection of Sampling Equipment and Analytical Instruments.

Table 9. Instruments Requiring Calibration.

Instrument	Analyte	Calibration Type	SOP Reference
Horiba U-22XD	Temperature, Conductivity, pH, and Turbidity	Automated / Manual	1050R01 Horiba U-22
Spectrophotometer	Total P and Total N	Calibration Curve	3010R01 TotalP



Figure 1. Organizational chart showing lines of authority and reporting responsibilities.



Figure 2. Niangua River Basin

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Single Flow = Dye injection point traced back to Bennett Spring Split Flow = Dye injection point traced back to multiple springs including Bennett Spring Figure 3. Bennett Spring Recharge Area Sample Sites

APPENDIX A. Standard Operating Procedures (SOPs) cited in this document.

Document Number	Title	Status
1030R01 Chain of Custody	Chain of Custody	Final
1040R01 Water Sampling	Water Sample Collection	Final
1050R01 Horiba U-22	Horiba U-22XD Multi- Parameter Water Quality Monitoring System	Final
3010R01 Total P	Total Phosphorus	Final
3020R01 Total N	Total Nitrogen	Final
6010R01 Ecoli IDEXX	<i>Escherichia coli</i> using the IDEXX Quanti-Tray/2000 System with Colilert reagent	Final
2060R01 Flow Meter	Operation of the Global Water Flow Meter Model FP201	Final
2050R01 Flow Discharge	Low Flow Velocity and Discharge	Final