Quality Assurance Project Plan for

Nonpoint Source and Water Quality Trends in the Pearson Creek Watershed

The Ozarks Environmental and Water Resources Institute (OEWRI)

Missouri State University

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PROJECT MANAGEMENT

Project and Task Organization

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

Problem Definition and Background

Pearson Creek Watershed is located east of Springfield, Missouri and drains 61 km² at its confluence with the James River (MDNR, 2004) (Figure 2). The watershed is composed of mixed agricultural, urban, and forest land uses and there are management concerns that nonpoint and industrial releases may be degrading aguatic life in lower Pearson Creek (MDNR, 2005). In particular, macroinvertebrate communities are impaired in the stream segment below Jones Spring in the lower Pearson Creek. Jones Spring issues from karst fractures and receives runoff inputs from an urbanized section of Springfield. Drinking water supply may also be at risk since Pearson Creek discharges into the James River about 1 km upstream of the Blackman municipal drinking water intake and then flows into Springfield Lake (USGS, 2005). Pearson Creek is listed on the 303d for unknown toxicity initiated by aquatic invertebrate species monitoring by City Utilities of Springfield (Youngsteadt, 1995). Additional water quality studies have been conducted by the US Geological Survey (USGS) and the Missouri Department of Natural Resources both of which were unable to determine a specific toxicant responsible for the decline in aquatic life in the Creek (Richards and Johnson, 2002; MDNR, 2005). To date, few of the water samples collected from Pearson Creek have exceeded state standards set to protect aquatic life. However, some samples have yielded total nitrogen levels above the James River TMDL limit of 1.5 mg/l TN (MDNR, 2005). In addition, monitoring by local groups has shown that bacteria levels in Pearson Creek exceed state standards periodically. The City of Springfield modified its stormwater monitoring efforts in 2004 to include toxicity testing that identifies potentially toxic pollutants not usually monitored.

A USEPA Region 7 – Federal Assistance Grant: "Water and Sediment Research Project for the Ozarks Environmental and Water Resources Institute at Missouri State University" was received by Dr. Robert Pavlowsky in 2006 to improve scientific understanding of water resource quantity, quality, and distribution in the Ozarks for protection and restoration purposes. This

QAPP supports one activity of this project that involves a water quality monitoring study on Pearson Creek aimed to address: (1) water and sediment quality problems in the Ozarks, (2) watershed initiatives of the USEPA, and (3) water quality goals of the Missouri Department of Natural Resources (MDNR). This QAPP focuses on the monitoring project entitled, "Nonpoint Source and Water Quality Trends in the Pearson Creek Watershed." It involves a watershed-scale water and sediment study of Pearson Creek to address unknown toxicity and nonpoint pollution sources including nutrients, metals, and bacteria to support efforts to develop a Total Maximum Daily Load (TMDL) by 2009.

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PROJECT AND TASK DESCRIPTION

Project Schedule and Time Line

Sampling sites were selected and personnel were trained to complete laboratory and field procedures from August 2007 to December 2007. See Table 2 for project schedule and time line.

The monitoring phase of this project will begin February 2008 and will end April 2009, spanning 14 months. Water sampling for this study includes both fixed-interval and storm-chasing water sampling. All sites with flow will be sampled once every two weeks. It is expected that only eight sites will provide enough flow for sampling during dry periods. Fixed-interval sampling often under-represents storm influences on water quality, therefore, storm runoff events will be targeted at a maximum frequency of one event per week and not to exceed two events per month. All sites with flow during storm events will be sampled. See Table 3 for site identification, flow conditions, drainage area, and land use.

Water quality indicators that will be measured in water samples collected are listed in Table 4. All indicators will be collected during fixed-interval and storm-chasing sampling except for bacteria and microbial source tracking samples which will only be collected during fixed-interval sampling. Discharge will be measures with a flow meter or a velocimeter periodically to provide calibration data for permanent staff gages installed at each site.

Data processing will involve the creation of concentration and load frequency relationships using the load-duration curve method. Water quality trends will be examined in relation to upstream watershed characteristics including land use, known point sources, and historical disturbance history. The goal of this project is to determine annual pollutant loads for each site and explain the causes of variations in pollution loads by source location and intensity. The final report will be completed by December 15, 2009.

Sampling Sites and Frequency

The sampling sites were selected based on accessibility for sampling, suitability for the project, size, water volume in the channel during baseflow conditions, location in the basin, and landuse distribution within the basin. Table 3 summarizes the sample sites selected for this project. The sampling sites are illustrated in Figure 3.

Nutrient, metal, and total suspended solid samples will be collected and staff gage, pH, temperature, conductivity, dissolved oxygen, and turbidity data will be gathered during fixed-interval and storm-chasing sampling. Bacteria and microbial source tracking samples will only be collected during fixed-interval sampling. Table 4 summarizes the sampling techniques for all analytes of interest.

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Work Schedule for Sample Collection and Analysis

Water samples for nutrient, metal, and total suspended solid analyses and water parameter data will be collected during fixed-interval and storm-chasing sampling at all sites with flow. Bacteria and microbial source tracking samples will only be collected during fixed-interval sampling.

Water samples will be collected for total phosphorus, total nitrogen, total lead, total copper, total zinc, and total suspended solids. Both total nutrient samples and total metal samples will be collected in separate 500ml bottles, acidified based on the analyte of interest, transported on ice, transferred to the laboratory with a chain of custody form, and analyzed prior to appropriate hold times. Total suspended solid samples will be transported on ice, transferred to the laboratory with a chain of custody form, and analyzed prior to appropriate hold times. The data from all analyses will be processed by the OEWRI QA/QC coordinator, recorded in a spreadsheet, and stored in the OEWRI office.

Bacteria samples will be collected using Thio-bags during fixed-interval sampling. Samples will be analyzed for *Escherichia coli* and total coliform using the IDEXX Quanti-Tray/2000 system. The data will be stored on bench sheets and will be organized in a spreadsheet kept in the OEWRI office.

Microbial source tracking samples will be collected using Whirl-Pak[®] bags during fixed-interval sampling. Samples will be analyzed for host specific *Bacteroides* through extraction, electrophoreses, and comparison procedures. Results will be recorded using a Kodak UV analyzer. Bench sheets and copies of the UV analyzer data will be stored in the OEWRI office.

Water chemistry parameters will be collected using the Eureka Amphibian Manta multiprobe at each site each time that samples are collected. This data will be stored on the PDA associated with the instrument and downloaded in the laboratory. Additional copies of the data will be stored in the OEWRI office.

Discharge for each site will be determined by recording the flow stage from the staff gage installed at each sampling site. Staff gage stage and discharge relationships will be determined by hydraulic equations (Weir-type or slope-area Mannings). Discharge data will be collected using the Global Water Flow Meter or the Son Tek/YSI FlowTracker Handheld Acoustic Doppler Velocimeter (ADV) at each site throughout the sampling period to calibrate rating curves. Average flow data will be collected using the flow meter and recorded in the Pearson NPS field book and compiled in a spread sheet in the laboratory. The velocimeter collects location, water depth, and velocity data within each station of a cross section and automatically computes discharge for each site. Site specific data will be downloaded from the ADV and entered into a spread sheet in the laboratory. All data will be used to produce a discharge calibration report that will be included in the final project report.

All data derived for this project will be reviewed by the analyst, the OEWRI QA/QC coordinator, and by the project supervisor. All data will be stored in Excel and Word 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). The project supervisor will forward project information to additional parties.

Target Water Quality Indicators

Field measured parameters:

1. Temperature (SOP: 1200R02 Eureka Snapshot): 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 Eureka Amphibian with Manta.

2. Conductivity (SOP: 1200R02 Eureka Snapshot): 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 Eureka Amphibian with Manta.

3. pH (SOP: 1200R02 Eureka Snapshot): 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 Eureka Amphibian with Manta.

4. Turbidity (SOP: 1200R02 Eureka Snapshot): 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 Eureka Amphibian with Manta.

5. Dissolved Oxygen (SOP: 1200R02 Eureka Snapshot): 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. Data will be collected using the Eureka Amphibian with Manta.

6. Discharge (SOPs: Flowmeter R01 and Velocimeter R01): Discharge indicates basin characteristics such as landuse, soil type, slope, and size and illustrates the basins response to precipitation events. Generally as discharge increases the river's capacity to carry sediments increases and pollutants can be suspended by certain flows. A rating curve will be established for each site to predict discharge based on staff gage stage. Standard engineering equations for estimating discharge will be used and discharge will be verified through field measurements using a propeller style flowmeter and a velocimeter.

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Laboratory measured analytes:

1. Total Phosphorus (SOP: 3010R01 Total P): Nutrients promote aquatic plant growth such as algae in waterways which can increase turbidity and deplete dissolved oxygen which can be detrimental to a healthy aquatic biological community. All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion. Digested samples are compared to colorimetric assay absorbance readings from a spectrophotometer and those absorbances are used to determine TP concentrations.

2. Total Nitrogen (SOP: 3020R01 Total N): Nutrients promote aquatic plant growth such as algae in waterways which can increase turbidity and deplete dissolved oxygen which can be detrimental to a healthy aquatic biological community. Total nitrogen is a measure of organic nitrogen, ammonia, nitrite, and nitrate nitrogen. Digested samples are compared to colorimetric assay absorbance readings from a spectrophotometer and those absorbances are used to determine TN concentrations.

3. Total Lead (SOP: Micro Total Trace Metals and ICP metals): Metals bind to sediments and can dissolve into the aquatic environment where organisms are in close and prolonged contact with the soluble metals which can lead to bioaccumulation throughout the food chain. Samples undergo a multi-elemental acid leach digestion and metal concentrations are determined by Inductively Coupled Plasma – Optical Emissions Spectroscopy (ICP-OES) measurement of ionic emission spectra.

4. Total Copper (SOP: Micro Total Trace Metals and ICP metals): Metals bind to sediments and can dissolve into the aquatic environment where organisms are in close and prolonged contact with the soluble metals which can lead to bioaccumulation throughout the food chain. Samples undergo a multi-elemental acid leach digestion and metal concentrations are determined by Inductively Coupled Plasma – Optical Emissions Spectroscopy (ICP-OES) measurement of ionic emission spectra.

5. Total Zinc (SOP: Micro Total Trace Metals and ICP metals): Metals bind to sediments and can dissolve into the aquatic environment where organisms are in close and prolonged contact with the soluble metals which can lead to bioaccumulation throughout the food chain. Samples undergo a multi-elemental acid leach digestion and metal concentrations are determined by Inductively Coupled Plasma – Optical Emissions Spectroscopy (ICP-OES) measurement of ionic emission spectra.

6. *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.

7. 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.

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8. Microbial Tracking (SOP: DNA): When the source of bacteria contamination in a water body is known the decision-making processes involved with water quality management are facilitated. DNA is extracted from filtered samples which undergoes agarose gel electrophoreses and visual comparison to a DNA ladder for bacteria source determination.

9. Total Suspended Solids (SOP: TSSolids): Total suspended solids, such as silt, decaying plant and animal matter, industrial wastes, and sewage, can effect stream health and aquatic life. Nutrients, pesticides, and metals that bind to solids on land are released when the solids are suspended in a water body increasing concentrations of pollutants in the water. Filter mass differential calculations are used to determine the total suspended solids in each sample.

Quality Objectives and Criteria for Measurement Data

The objective of this project is to determine nonpoint pollutant loads and describe source locations in the Pearson Creek Watershed. Data collected will be used for comparison among sites to assess the spatial variability of water quality within the watershed. All field and laboratory analytical data are evaluated based on established measurement performance criteria as listed in Table 5.

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 5).

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<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 Pearson Creek 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 5)

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).

Documents and Records

The documents and records produced for this project will be stored in the OEWRI office in a file entitled: "Pearson NPS". 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 a system in place to automatically backup all data files.

<u>Quality Assurance Project Plan (QAPP)</u>: This document will be updated as needed by the QA/QC coordinator. The USEPA project supervisor, through the project supervisor, 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/QC coordinator 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/QC coordinator. 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 USEPA project supervisor must review all reports, presentations, media releases, etc. prior to publication or distribution. These items must be sent to the project management who will forward the information to the USEPA project manager.

DATA GENERATION AND ACQUISITION

Sampling Process Design

The objective of this project is to assess nonpoint pollutants in the Pearson Creek Watershed by conducting a comprehensive water quality monitoring study. The 15 sampling sites for the project were chosen based on accessibility, water volume in the channel, location in the basin, and landuse distribution. Analtyes include total nitrogen, total phosphorus, total lead, total cooper, total zinc, *Escherichia coli,* total coliform, and total suspended solids. Water quality parameters include pH, temperature, conductivity, dissolved oxygen, and turbidity. Data will be used to compare sites to assess the spatial variability of water quality within the watershed.

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Sampling Methods

Surface water samples for nutrient analysis will be collected by the grab sampling technique (SOP: 1040R01 Water Sampling.doc) using 500 mL plastic bottles from flowing water. One duplicate sample will be taken during each sampling event. Bottles will be cleaned using procedures included in the Preparation of Sample Bottles For non-Metals Analyses (SOP: 0150R01 Bottle Prep non-Metals) prior to sampling events. Samples will be preserved with sulfuric acid to a pH \leq 2, placed on ice during transport, transferred to the laboratory with appropriate chain of custody forms, and analyzed prior to hold times. Sample bottles will be cleaned and reused.

Surface water samples for metal analysis will be collected by the grab sampling technique (SOP: 1040R01 Water Sampling.doc) using 500 mL plastic bottles from flowing water. One duplicate sample will be taken during each sampling event. Bottles will be cleaned using procedures included in the Preparation of Sample Bottles For Metals Analyses (SOP: 0150R01 Bottle Prep Metals) prior to sampling events. Samples will be preserved with trace metal grade nitric acid to a pH \leq 2, placed on ice during transport, transferred to the laboratory with appropriate chain of custody forms, and analyzed prior to hold times. Sample bottles will be cleaned and reused.

Surface water samples for bacteriology analyses will be collected by the grab sampling technique (SOP: 4010R01 Ecoli IDEXX.doc) from flowing water. The 100 mL Thio-Test bags are either dipped into the stream by hand or at the end of a sampling pole. One duplicate sample will be taken during each sampling event. Care should be taken to not skim the surface while collecting samples. Samples will be placed on ice during transport, transferred to the laboratory with appropriate chain of custody forms, and processed immediately upon returning to the laboratory. The bacteriology Thio-Test bags are sterilized by the manufacturer and will be discarded after use.

Surface water samples for microbial source tracking analyses will be collected by the grab sampling technique (SOP: DNA.doc) from flowing water. The 500 mL Whirl-Pak bags are either dipped into the stream by hand or at the end of a sampling pole. One duplicate sample will be taken during each sampling event. Samples will be placed on ice during transport, transferred to the laboratory with appropriate chain of custody forms, and processed immediately upon returning to the laboratory. Transport will not exceed 3 hours. The Whirl-Pak bags are sterilized by the manufacturer and will be discarded after use.

Surface water samples for total suspended solids will be collected by the grab sampling technique (SOP: 1040R01 Water Sampling.doc) using 500 mL plastic bottles from flowing water. One duplicate sample will be taken during each sampling event. Samples will be placed on ice during transport, transferred to the laboratory with appropriate chain of custody forms, and analyzed prior to hold times. Samples are not preserved with acid. Sample bottles will be cleaned and reused.

A Eureka Amphibian Manta multiprobe (SOP: 1200R02 Eureka Snapshot.doc) will be used to collect pH, temperature, conductivity, dissolved oxygen, and turbidity data in the field. One duplicate reading for each parameter will be taken at one site during each sampling event. Sites chosen for duplicate readings will vary.

A rating curve will be established to predict discharge based on staff gage stage at all but one of the sites. Each monitoring site was visited and surveyed for channel dimensions and bed slope which was used to calculate the capacity of the channel, culvert, or pipe. Standard equations (Broad-Crested Weir, Manning Equation, and Continuity Equation) were used to estimate discharge for each site using a flow depth in 0.1 meter depth intervals for metal staff gages installed at each site. Discharge rating curves were created using the gage depth – discharge relationship for each site for the range of flow expected at each site. Equations from rating curves will be used to estimate discharge based on the staff gage stage that will be collected at each site each time that samples are collected at the site. Because there are inherent errors in estimating discharge from equations, the rating curve will be calibrated with field measurements of discharge at each site. A minimum of three flow measurements at low, moderate, and high stages at each site will be used to calibrate each rating curve. Flow measurements will be collected using two types of methods. During baseflow, when the water level is relatively low, an Acoustic Doppler Velocimeter (ADV) (SOP: Velocimeter R01) will be used. During storm events, when the water is relatively high, a propeller style flowmeter (SOP: Flowmeter R01) will be used to measure an average velocity. One site has a United States Geological Survey (USGS) gage already in place that provides real-time discharge data via the internet. See Table 6 for site information used during discharge determinations. The final project report will include discharge calibration report.

Sample Handling and Custody

See Table 7 for sample handling conditions for each analyte of interest for this project.

Water quality parameter data is stored on the PDA associated with the Eureka Amphibian with Manta. The data will be transferred from the PDA to the laboratory computer upon return to the laboratory. Field measurements for discharge calibration will be recorded on bench sheets provided in the SOPs associated with that determination or in the Pearson Creek field notebook.

Water samples are collected in appropriate bottles or bags for each parameter. A label will be affixed to or written on each container and will contain the following information: date and time of collection, site code, project, list of analytes, and sample collector's initials (SOP: 1040R01 Water Sampling.doc). 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.

A Sample Collection form 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 5 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 QA/QC coordinator and/or the project management. Corrections will be made and samples reanalyzed if possible. The problem will be documented in the instrument log book.

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 stated requirements. Quality control activities ensure that measurement systems are maintained within prescribed limits and that results are of acceptable quality.

The quality control checks used in this project are listed in Table 5. Field and laboratory blanks and duplicates will be used as a check for precision. Matrix spikes, check standards, and calibration standards are used to measure bias and accuracy. Sensitivity is determined by analyzing equipment blanks and reagent blanks.

One field blank will be collected during each sampling event. One field duplicate will be collected for every ten samples collected. Laboratory duplicates will be analyzed at a frequency of one per 10 samples analyzed. Two laboratory spiked samples will be analyzed for every batch of samples analyzed. The laboratory blank and check standards will be analyzed after every 10 samples analyzed.

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. The analyst is responsible for understanding when the analytical process is out of control. See Table 8 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 established 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.

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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 9 for a list of instrumentation and equipment and the approximate schedule for preventive maintenance. Preventive maintenance procedures are also listed in the 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 (check) standard will be after every 10 samples during the analytical run. A verification (check) standard will be acceptable if its value is within $\pm 10\%$ of the expected value.

See Table 10 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 of interest.

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.

Sample bottles used to collect nutrient and total suspended solid samples will be reused throughout the sampling period. The sample bottles will be emptied, rinsed with tap water, washed with a 2% solution of Citranox, rinsed with deionized water (DI), soaked in 10% hydrochloric acid overnight and rinsed with DI again. The bottles are allowed to drain dry and then are stored in sealed plastic bags until use. Two bottles from each batch of washed bottles are filled with DI water and analyzed for TP and TN

residues using the nutrient analysis procedures (SOPs: 3010R01 Total P.doc and 3020R01 Total N.doc). The hydrochloric acid solution will be tested by the cleanliness of the bottles. If the bottles show no TP or TN residual, then the acid solution will be considered "clean" enough for this procedure. The solution will not be re-used beyond two months after its preparation.

Sample bottles used to collect metal samples will be reused throughout the sampling period. The sample bottles will be emptied, rinsed with tap water, washed with a 2% solution of Citranox, rinsed with deionized water (DI), soaked in 25% nitric acid overnight and rinsed with DI again. The bottles are allowed to drain dry and then are stored in sealed plastic bags until use. Two bottles from each batch of washed bottles are filled with DI water and analyzed for metal residues using the metal analysis procedures (SOPs: Micro Total Trace Metals.doc and ICPmetals.doc). The nitric acid solution will be tested by the cleanliness of the bottles. If the bottles show no metal residual, then the acid solution will be considered "clean" enough for this procedure. The solution will not be re-used beyond two months after its preparation.

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.

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

One non-direct discharge measurement is required for this project. That measurement will be taken from the USGS website for site M6.

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. The 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 and will be titled "Pearson NPS". 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.

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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 stored in the PDA associated with the Eureka Amphibian with Manta will be downloaded to the laboratory computer file titled "Pearson NPS". Raw instrument data will be stored in the Eureka Multiprobe Manager folder of the QC coordinator's computer as well. The raw data will be transferred to an Excel file for processing and review. A second copy of all processed data will be stored on the Pearson NPS removable drive. All data printouts will be stored in the project file in the OEWRI office.

Laboratory Instrumentation: Data internally stored on a computer associated with a laboratory instrument will be saved to the file titled "Pearson NPS". Raw instrument data will be stored in a Pearson NPS folder of the QC coordinator's computer as well. The raw data will be transferred to an Excel file for processing and review. A second copy of all processed data will be stored on the Pearson NPS removable drive. All 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/QC coordinator.

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 QC Coordinator will review with the project Graduate Assistants 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 transfer data after it is generated.

<u>Proficiency Testing</u>: A sample with a known-concentration of analyte 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/QC coordinator 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/QC coordinator 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 sampling period. 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 QC coordinator. These may be issued as e-mail messages or as a Word or Excel file in an e-mail attachment. Copies of all reports will be stored in the project file in the OEWRI office. Project management will forward information to outside agencies.

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 QC coordinator, and project management will review all data.

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<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, QC coordinator, project management, 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 assess nonpoint pollutants in the Pearson Creek Watershed by conducting a comprehensive water quality monitoring study. These goals will be met by processing data generated by following the procedures outlined in this QAPP and specifically stated in associated SOPs. The final report will include descriptions of water quality results found at each site and spatial and temporal trends will be identified where seen. Recommendations will be made for future studies based on pollutant concentrations and trends.

Literature Cited

Missouri Department of Natural Resources. Total Maximum Daily Load Information Sheet, Pearson Creek. December 2004. www.dnr.mo.gov/env/wpp/tmdl/info/2373-pearson-ck-info.pdf

- Richards, J.M., and T.B. Johnson. 2002. Water Quality, Selected Chemical Characteristics, and Toxicity of Base Flow and Urban Stormwater in the Pearson Creek and Wilsons Creek Basin, Greene County, Missouri, August 1999 to August 2000. U.S. Geological Survey Water Resources Investigations Report 02-4124.
- United States Geological Survey. Wilson and Pearson Creek Stormwater Project January 12, 2005. http://mo.water.usgs.gov/current_studies/richards/spfd/spfd2.htm
- Youngsteadt, N.W. 1995. The Deterioration of the Macroinvertebrate Fauna of Lower Pearson Creek Along the Eastern Edge of Springfield, Missouri With Comparison to Other Local Sampling Points Under Varying Influence From the City of Springfield. City Utilities, Springfield, Missouri.

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 OEWRI Laboratory Director/ Project Supervisor | OEWRI | Project coordination and QA/QC coordination regarding laboratory procedures. | 417-836-3198 hhoggard@MissouriState.edu | 2 |
| Marc Owen Research Specialist II/ Discharge Coordinator | OEWRI | Staff gage plan and calibration report. | 417-836-3197 MOwen@MissouriState.edu | 3 |
| Derek Martin Research Specialist GIS Manager | OEWRI | Mapping, GIS functions. | 417-836-3015 DJMartin@MissouriState.edu | 4 |
| Dr. Jack Steiert, MSU Faculty | MSU Biology | Supervise bacteria analyses. | 417-836-6916 JohnSteiert@MissouriState.edu | 5 |
| Dr. Richard Biagioni, MSU Faculty | MSU Chemistry | Supervise chemistry analyses. | 417-836-4649 <u>RNBiagioni@MissouriState.edu</u> | 6 |
| Regina Kidwell, USEPA Region 7 Administration, KC | United Stated Environmental Protection Agency | USEPA Oversight, KC | 913-551-7788 kidwell.regina@epa.gov | 7 |
| Jaci Ferguson, USEPA Region 7 Administration, Springfield | United States Environmental Protection Agency | USEPA Oversight, Springfield | 417-575-8028 ferguson.jaci@epa.gov | 8 |

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| Name and Title | Organization | Responsibilities | Contact Information | QAPP Receipt/ Control number |
|--------------------------------------|---|---|---|---------------------------------------|
| Diane Harris, USEPA QA Manager | United States Environmental Protection Agency | USEPA QA Oversight | 913-551-7258 harris.dianee@epa.gov | 9 |
| Brian Swift Graduate Assistant | MSU | Collect and analyze samples, record maintenance, reporting. | 417-836-8705 swift000@MissouriState.edu | 10 |
| Anthony Saitta Graduate Assistant | MSU | Collect and analyze samples, record maintenance, reporting. | 417-836-8705 Saitta311@MissouriState.edu | 11 |

Table 2. Project Schedule Time Line.

| Activity | Date (MM/DD/YYYY) | | | Deliverable Due Date | |
|---|------------------------|--------------------------------|--------------------------|-------------------------|--|
| | Anticipated Start Date | Anticipated Completion Date | Deliverable | | |
| Select sampling sites | 08/01/2007 | 10/01/2007 | Approved sample site map | 12/7/2007 | |
| Laboratory Analysis Training/Discharge and Gage Calibration | 08/01/2007 | 12/31/2007 | Memo | 12/31/2007 | |
| Bi-Monthly Water Chemistry Sampling and Storm Chasing | 02/01/2008 | 04/30/2009 | Memo | 04/30/2009 | |
| Data Processing | 04/30/2009 | 09/31/2009 | Memo | 09/31/2009 | |
| Final Report | 09/31/2009 | 12/15/2009 | Report | 12/15/2009 | |

| Site ID | Location | UTM Northing | UTM Easting | Flow Conditions | Drainage Area (km2) | % High Den Urban | % Low Den Urban | % Barren | % Crops | % Grass | % Forest | % Water |
|---------|--|---------------|--------------|--------------------|---------------------------|---------------------------|--------------------------|-------------|------------|------------|-------------|------------|
| M1 | Box culvert at SH OO ds of I44 | 4123522.19517 | 486533.31783 | Ephemeral | 4.4 | 5 | 3.9 | 2.4 | 17.9 | 55.2 | 15.3 | 0.3 |
| T1 | 2 cell box culvert on Spring Trib at FR 213 | 4121522.61925 | 486717.72696 | Perennial | | | | Spring | g | | | |
| M2 | 3 cell box culvert on FR 213 | 4121400.53863 | 486639.02496 | Perennial | 13.3 | 5.7 | 5.7 | 1.9 | 8.7 | 68.9 | 8.9 | 0.2 |
| T2 | 2 cell box culvert FR 116 | 4121182.43579 | 484905.13006 | Ephemeral | 1.9 | 4.7 | 18.1 | 0 | 11.2 | 56 | 9.7 | 0.3 |
| M3 | Bridge at SH YY | 4119560.78905 | 484842.28041 | Perennial | 25.8 | 3.4 | 4.7 | 1.2 | 8.2 | 70.7 | 11.4 | 0.3 |
| Т3 | Arched culvert at SH YY east of main channel | 4119591.42812 | 484171.59435 | Ephemeral | 1.6 | 1 | 12.9 | 0 | 0.1 | 73 | 13 | 0 |
| T4 | 2 cell box culvert on Pearson Meadow Lane | 4118849.23309 | 481820.29250 | Ephemeral | 6.0 | 8 | 9.1 | 0 | 6.1 | 71.5 | 5.2 | 0 |
| M4 | 4 barrel culvert on FR 193 | 4117844.43832 | 482370.44037 | Perennial | 33.9 | 2.9 | 5.1 | 1 | 7.5 | 69.3 | 13.9 | 0.3 |
| T5 | 2 barrel culvert on FR 193 | 4116296.04848 | 482412.88941 | Ephemeral | 1.9 | 2 | 29.1 | 0.1 | 0.3 | 42.1 | 26.5 | 0 |
| M5 | Bridge at FR 144 | 4115674.97305 | 482244.35293 | Perennial | 48.6 | 3.8 | 9.2 | 0.7 | 6 | 65.2 | 14.9 | 0.3 |
| Т6 | Pond Control Structure at Leaning Tree Lane | 4115616.08981 | 482112.41964 | Ephemeral | 3.2 | 19.6 | 48.1 | 0 | 0.9 | 16.5 | 13.8 | 1.1 |
| M6 | Bridge at FR 148 s of SH D | 4114633.63151 | 482384.73405 | Perennial | 53.4 | 4.7 | 12.4 | 0.6 | 5.5 | 61.2 | 15.2 | 0.4 |
| T7 | Box culvert on Deer Run lane | 4114231.38410 | 482341.89238 | Ephemeral | 2.0 | 22.2 | 35.8 | 0 | 0.3 | 24.7 | 16.9 | 0 |
| M7 | Box culvert on FR 193 | 4114039.47091 | 482562.42928 | Perennial | 55.5 | 5.4 | 13.7 | 0.6 | 5.3 | 59.4 | 15.2 | 0.3 |
| M8 | At John Hopkins property near the confluence | 4113471.08880 | 482613.03404 | Perennial | 57.9 | 6 | 14.4 | 0.6 | 5.1 | 57.9 | 15.7 | 0.3 |

Table 3. Sample Site Summary

Coordinate system = UTM NAD83 Zone 15 Perennial = Flow throughout entire year Ephemeral = Flow during storms or precipitation events Spring = Outflow of the Jones Spring

Table 4. Sampling Techniques

| Sampling Device or Procedure | Collected By | Sites | Location | Number collected | Analytes |
|---------------------------------|-------------------|-------------------------------------|----------|--|------------------------|
| Manual Grab Sample | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | Nutrients |
| Manual Grab Sample | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | Metals |
| Manual Grab Sample | Project Assistant | Permanent Sites | Stream | Fixed-Interval = 2 per month | Bacteria |
| Manual Grab Sample | Project Assistant | Permanent Sites | Stream | Fixed-Interval = 2 per month | Microbial Tracking |
| Manual Grab Sample | Project Assistant | Permanent Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | Total Suspended Solids |
| In situ | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | Temperature |
| In situ | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | рН |

| In situ | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | Conductivity |
|---------|-------------------|-------------------------------------|--------|--|------------------|
| In situ | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | D.O. |
| In situ | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | Turbidity |
| In situ | Project Assistant | Permanent and Ephemeral Sites | Stream | Fixed-Interval = 2 per month Storm-chasing = up to 2 per month | Staff Gage Stage |

Table 5. Measurement Performance Criteria.

| Matrix = Water | Sampling Procedure = 0 | Grab Sample | | |
|----------------|------------------------|------------------------|-------------------------------------|--|
| Parameter | SOP | Data Quality Indicator | Measurement Performance Criteria | QC Sample Type to assess Measurement Performance |
| Total Nitrogen | 3020R01 TotalN | Accuracy | ± 20% | LB, LS |
| | | Bias | ± 20% | LB, LS |
| | | Precision | ± 20% RPD | LD |
| | | Sensitivity | ≤ 0.1 mgN/L | MDL, LRB |

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| Matrix = Water Sampling Procedure = Grab Sample | | | | |
|---|-------------------------------------|-------------|-------------------------------------|--|
| Parameter | arameter SOP Data Quality Indicator | | Measurement Performance Criteria | QC Sample Type to assess Measurement Performance |
| Total Phosphorus | 3010R01 TotalP | Accuracy | ± 20% | LB, LS |
| | | Bias | ± 20% | LB, LS |
| | | Precision | ± 20% RPD | LD |
| | | Sensitivity | ≤ 0.005 mgP/L | MDL, LRB |
| Total Metals (Pb, Cu, Zn) | Micro Total Trace Metals | Accuracy | ± 20% | LB, LS |
| | ICP metals | Bias | ± 20% | LB, LS |
| | | Precision | ± 20% RPD | LD |
| | | Sensitivity | Metal and Matrix Dependent | MDL, LRB |
| Escherichia coli | 6010R01 Ecoli IDEXX | Accuracy | NA | ND |
| | | Bias | NA | ND |
| | | Precision | ± 20% RPD | FD, LD |
| | | Sensitivity | 1 MPN/100mL | LRB |
| Microbial Tracking | DNA | Accuracy | DNA Ladder Used | LB |
| | | Bias | NA | LB |
| | | Precision | Base Pair Specific | FD, LD |
| | | Sensitivity | Base Pair Specific | LRB |
| Total Suspended Solids | TSSolids | Accuracy | ± 20% | LB |
| | | Bias | ± 20% | LB |
| | | Precision | ± 20% RPD | LD |

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| Matrix = Water | Sampling Procedure | Sampling Procedure = Grab Sample | | |
|------------------|--------------------|----------------------------------|-------------------------------------|--|
| Parameter | SOP | Data Quality Indicator | Measurement Performance Criteria | QC Sample Type to assess Measurement Performance |
| | | Sensitivity | ≤ 0.5 mg/L | MDL, LRB |
| рН | Eureka Snapshot | Accuracy | ± 20% | Reference standard |
| | | Bias | ± 20% | Reference standard |
| | | Precision | ± 20% RPD | LD, FD |
| | | Sensitivity | 1 unit | NA |
| Temperature | Eureka Snapshot | Accuracy | NA | ND |
| | | Bias | NA | ND |
| | | Precision | ± 20% RPD | FD, LD |
| | | Sensitivity | 0º C | Ice bath |
| Conductivity | Eureka Snapshot | Accuracy | ± 20% | LB, LS |
| | | Bias | NA | ND |
| | | Precision | ± 20% RPD | FD, LD |
| | | Sensitivity | 0 mS/m | LRB |
| Dissolved Oxygen | Eureka Snapshot | Accuracy | ± 20% | LB, LS |
| | | Bias | NA | ND |
| | | Precision | ± 20% RPD | FD, LD |
| | | Sensitivity | 0 mS/m | LRB |
| Turbidity | Eureka Snapshot | Accuracy | ± 20% | LFB |
| | | Bias | ± 20% | LFB |
| | | Precision | ± 20% RPD | LD, FD |

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| Matrix = Water | Sampling Procedure = 0 | Grab Sample | | |
|----------------|------------------------|------------------------|-------------------------------------|--|
| Parameter | SOP | Data Quality Indicator | Measurement Performance Criteria | QC Sample Type to assess Measurement Performance |
| | | Sensitivity | 1 NTU | LRB |

*LB = Laboratory Blank (reference sample), LM = Laboratory Spike

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

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| Site ID | Structure/Channel Type and Location | Structure/Channel Size | Stage Measurement | Q Equation Used |
|---------|--|--|-------------------|--------------------|
| M1 | Box culvert at SH OO ds of I44 w/ concrete floor | W = 2.23 m D = 1.23 m S = 1 % | Stage Gage | Manning |
| T1 | 2 cell box culvert on Spring Trib at FR 213 w/ concrete floor | W = 1.24 m D = 0.64 m S = 1.54 % | Stage Gage | Manning |
| M2 | 4 cell box culvert on FR 213 w/ concrete floor | W = 1.86 m D = 1.22 m S = 1 % | Stage Gage | Manning |
| T2 | 2 cell box culvert FR 116 w/ concrete floor | W = 2.43 m D = 1.52 m S = 2.6 % | Stage Gage | Manning |
| M3 | Bridge at SH YY, concrete sides and natural bottom | W = 2.23 m* D = 1.23 m* S = 0.07 % | Stage Gage | Manning |
| Т3 | Culvert at SH YY east of main channel w/ natural bottom | W = 3.5 m D = 0.92 m S = 1 % | Stage Gage | Manning |
| T4 | 2 cell box culvert on Pearson Meadow Lane w/ concrete floor | W = 2.44 m D = 1.4 m S = 0.87 % | Stage Gage | Manning |
| M4 | 4 barrel corrugated metal pipe culvert on FR 193 | Dia = 1.23 m S = 0.17 % | Stadia Rod | Manning |
| T5 | 2 barrel corrugated metal pipe culvert on FR 193 | Dia = 1.8 m S = 0.9 % | Stadia Rod | Manning |
| M5 | Natural Channel at FR 144 Bridge | W = 12.3 m* D = 0.65 m* S = 0.33% | Stage Gage | Manning |
| Т6 | Broad Crested Weir Pond Control Structure at Leaning Tree Lane | WL = 4.12 m WH = 1.06 m | Stage Gage | Weir |
| M6 | Bridge at FR 148 s of SH D | n/a | Internet | USGS Gage |
| Τ7 | Box culvert on Deer Run lane w/ concrete floor | W = 2.23 m D = 1.23 m S = 0.19 % | Stage Gage | Manning |
| M7 | Box culverts on FR 193 w/ concrete floors | W = 2.45 m D = 1.2 m S = 1 % | Stage Gage | Manning |
| M8 | Natural channel At John Hopkins property near confluence | W = 18.7 m* D = 1.16 m* S = 1 % | Stage Gage | Manning |

Table 6. Site Information for Discharge Determination

W = width

D = mean depth

S = bed slope %

Dia = diameter WL = weir length

WH = total weir height

* = measurements at total channel capacity = top of bank Manning Equation (Ward and Elliot, 1995) = V = $1/n(R^{0.66})(S^{0.5})$ Broad-Crested Weir (Greene County Storm Water Design Standards, 1999) = Q = C(L)(H^{1.5})

| Table 7. | Sample | Collection | Conditions | for | Analytes | 5. |
|----------|--------|------------|------------|-----|----------|----|
|----------|--------|------------|------------|-----|----------|----|

| Analyte | Bottle Type | Bottle Size | Preservative | Holding time | SOP Reference |
|---|------------------|-----------------------|---|--------------|--------------------------|
| Total Nitrogen | Plastic | 500 ml | H₂SO₄ to pH ≤ 2 Ice | 28 days | 3020R01 TotalN |
| Total Phosphorus | Plastic | 500 ml | H₂SO₄ to pH ≤ 2 Ice | 28 days | 3010R01 TotalP |
| Total Metals (Pb, Cu, Zn) | Plastic | 500 ml | Trace Metal HNO ₃ to pH \leq 2 Ice | 6 months | Micro Total Trace Metals |
| E. coli | Thio-bag | 100 ml | Ice | 3 hours | 4010R01 Ecoli IDEXX |
| Microbes (Bac32F, CF128F, CF193F, HF183F) | Whirl-Pak bag | 500 ml | Ice | 3 hours | DNA |
| Total Suspended Solids | Plastic | 500 ml | Ice | 60 days | TSSolids |
| Field Parameters | These paramet | ters are collected ir | n situ. | | |
| рН | none | none | none | none | 1200R02 Eureka Snapshot |
| Temperature | none | none | none | none | 1200R02 Eureka Snapshot |
| Conductivity | none | none | none | none | 1200R02 Eureka Snapshot |
| Dissolved Oxygen | none | none | none | none | 1200R02 Eureka Snapshot |
| Turbidity | none | none | none | none | 1200R02 Eureka Snapshot |
| Velocity | none | none | none | none | Velocimeter R01 |

| 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 (LS) fails | If Reference sample (LS) is acceptable, then qualify the data If LS and LB fail, then re-prepare and reanalyze the affected samples. | These data are associated with a LS recovery result that is > UCL (or < LCL). | | | |
| Laboratory Blank (LB) fails | Analyze another LB. If 2nd LB 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 LB 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 = Lower Control Limit | | | | | |

| Equipment / Instrument | Maintenance, Testing, or Inspection Activity | Frequency | SOP Reference |
|---------------------------|--|------------------------------|-----------------|
| Sampling Equipmen | t | | |
| Manta | Auto Calibration | Before each use | Eureka Snapshot |
| | Cleaning | After each use | |
| | Manual Calibration | Monthly | |
| | Battery replacement | As needed | |
| | Rebuild DO Sensor, Recharge pH Probe | As needed | |
| Laboratory Equipme | ent | | |
| Spectrophotometer | Create calibration curve | For each use | 3010R01 Total P |
| Spectrophotometer | Create calibration curve | For each use | 3020R01 Total N |
| ICP-OES | Create calibration curve | For each use, for each metal | ICP metals |
| Velocimeter | Performance Check | Before each use | Velocimeter R01 |

Table 9. Maintenance, Testing, and Inspection of Sampling Equipment and Analytical Instrumentation.

Table 10. Instrumentation Requiring Calibration.

| Instrument | Analyte | Calibration Type | SOP Reference |
|-------------------|--|--------------------|-------------------------------------|
| Manta | pH, Conductivity, Dissolved Oxygen, and Turbidity | Automated / Manual | Eureka Snapshot |
| Spectrophotometer | Total P and Total N | Calibration Curve | 3010R01 Total P and 3020R01 Total N |
| Velocimeter | Discharge | ADVCheck software | Velocimeter R01 |



Pearson

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

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Figure 2. James River Basin.

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Figure 3. Pearson Creek Watershed and Sampling 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 |
| Eureka Snapshot | Eureka Amphibian and Manta Water Quality Multiprobe for Multiple Location parameter Measurement | Final |
| 3010R01 Total P | Total Phosphorus | Final |
| 3020R01 Total N | Total Nitrogen | Final |
| Micro Total Trace Metals | Microwave Digestion of Water Samples for the Determination of Total Trace Metal Concentration | Final |
| ICP metals | Using the Inductively Coupled Plasma – Optical Emissions Spectroscopy (ICP-OES) Instrument for the Determination of Trace Metal Concentration in Water, Sediment, or Organic Samples | Final |
| 6010R01 Ecoli IDEXX | Escherichia coli using the IDEXX Quanti-Tray/2000 System with Colilert reagent | Final |
| DNA | Microbial Source Tracking | Final |
| TSSolids | Total Suspended Solids | Final |
| Velocimeter R01 | Operation of the SonTek/YSI FlowTracker Handheld Acoustic Doppler Velocimeter (ADV) | Final |
| 2060R01Flow Meter | Operation of the Global Water Flow Meter, Model FP201 | Final |
| 0150R01 Bottle Prep non- Metals | Preparation of Sample Bottles For non-Metal Analyses | Final |
| 0100R01 Bottle Prep Metals | Preparation of Sample Bottles For Metals Analyses | Final |