

Quality Assurance Project Plan for

**Suspended Sediment and Dissolved Solid Transport
in the James River, SW Missouri**

The Ozarks Environmental and Water Resources Institute (OEWRI)

Missouri State University

**In support of the USEPA Region 7-Federal Assistance Grant number
(X7)98772501:**

**“Water and Sediment Research Project for the Ozarks Environmental
and Water Resources Institute at Missouri State University”**

September 2008



Prepared by:

Heather Hoggard, OEWRI Laboratory Director

Date

Marc Owen, OEWRI Research Specialist II

Date

Approved by:

Dr. Robert T. Pavlowsky, OEWRI Director, MSU
Faculty - GGP, Principal Investigator

Date

Regina Kidwell, Region 7 Administration, KC
United States Environmental Protection Agency

Date

Jaci Ferguson, Region 7 Administration, Springfield
United States Environmental Protection Agency

Date

Diane Harris, QA Manager
United States Environmental Protection Agency

Date

TABLE OF CONTENTS

Prepared by:	2
Approvals.....	2
List of Tables	4
List of Figures	4
Distribution List.....	5
PROJECT MANAGEMENT	6
Project and Task Organization	6
Problem Definition and Background.....	6
PROJECT AND TASK DESCRIPTION	7
Project Schedule and Time Line.....	7
Work Schedule for Sample Collection and Analysis	8
Sampling Sites and Frequency.....	9
Target Water Quality Indicators.....	9
Field measured parameters:	9
Laboratory measured analytes:	9
Quality Objectives and Criteria for Measurement Data	13
Data Quality Indicators, Definitions	13
Special Training and Certification.....	14
Documents and Records	14
DATA GENERATION AND ACQUISITION	15
Sampling Process Design.....	15
Sampling Methods.....	15
Sample Handling and Custody	16
Analytical Methods	17
Quality Control.....	17
Instrument and Equipment Testing, Inspection, and Maintenance.....	18
Instrument and Equipment Calibration and Frequency	18
Inspection and Acceptance of Supplies and Consumables	19
Non-direct Measurements.....	19
Data Management.....	19
ASSESSMENT AND OVERSIGHT.....	20
Assessments and Response Actions	20
Reports to Management.....	21
DATA VALIDATION AND USABILITY	21
Data Review, Verification and Validation.....	21
Verification and Validation Methods	22
Reconciliation with User Requirements	22
TABLES.....	24
FIGURES	35
APPENDIX A. Standard Operating Procedures (SOPs) cited in this document....	37
APPENDIX B. Flowchart of Sample Distribution for Analyses.....	38

List of Tables

Table 1. Personnel, Responsibilities and QAPP Receipt. 24
Table 2. Project Schedule Time Line..... 25
Table 3. Sample Site Summary..... 26
Table 4. Sampling Techniques 26
Table 5. Measurement Performance Criteria. 28
Table 6. Sample Collection Conditions for Analytes..... 31
Table 7. Quality Control Corrective Action Plan. (Standard Methods, 2005)..... 32
Table 8. Maintenance, Testing, and Inspection of Sampling Equipment and Analytical
Instrumentation. 33
Table 9. Instrumentation Requiring Calibration. 34

List of Figures

Figure 1. Organizational chart showing lines of authority and reporting responsibilities.
..... 35
Figure 2. James River Basin and Sampling Sites.....36

Distribution List

Regina Kidwell (913-551-7788)	United States Environmental Protection Agency Region 7 Administration, Kansas City
Jaci Ferguson (417-575-8028)	United States Environmental Protection Agency Region 7 Administration, Springfield
Diane Harris (913-551-7258)	United States Environmental Protection Agency QA Manager
Dr. Robert T. Pavlowsky (417-836-8473)	OEWRI Director, Principal Investigator
Heather Hoggard (417-836-3198)	OEWRI Laboratory Director, Project Supervisor
Marc R. Owen (417-836-3197)	OEWRI Research Specialist II, GIS Support
Dr. Richard N. Biagioni (417-836-4649)	MSU Chemistry Faculty
Dr. William A. Alter III (417-836-5972)	Director, MSU Office of Sponsored Research and Programs

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

The James River Basin is located in southwest Missouri and drains 987 square miles where it flows into the 43,100 acre Table Rock Lake at Galena, Missouri. The James River and its tributaries are listed on the modified 2004 303(d) list as being impaired by multiple point and non-point sources of the following pollutants with river mile miles affected: nutrients (59 mi), mercury (54 mi), and unknown toxicity (20 mi). The James River is ranked high on Missouri's Watershed Unified Assessment for nutrient pollution and the US Environmental Protection Agency (EPA) approved the James River Total Maximum Daily Load (TMDL) in 2001 which mainly focused on point sources of nutrients in the watershed. In addition, recent investigations by the James River Basin Partnership and Missouri State University have raised concerns about sediment, bacteria, and possibly metals contamination in the James River Basin and Table Rock Lake. These pollutants are listed as causes of impairment on the 303(d) list in surrounding basins as well. Efforts to control point sources over the past several years have reduced base flow nutrient concentrations in the Lower James River.

The EPA has recognized sediment as the primary nonpoint source pollutant in most water bodies, although few studies focus on sediment transport within the water column. Determining the dynamics of suspended sediment and dissolved solids transport in the upper and middle James River basin will improve our understanding of the source of pollutants in the basin and the degree of variation in concentrations of pollutants throughout the year due to runoff and seasonal influence. This study will focus on evaluating these parameters: suspended and dissolved solids; total and dissolved organic and inorganic carbon; fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfate; total nitrogen and total phosphorus; and water chemistry including dissolved oxygen, pH, specific conductivity, turbidity, and temperature. Presently, there are no studies available that adequately describe the dynamics of solids transport in karst-dominated Ozark watersheds and this information is vital for water quality management of the James River system including the lake arm areas.

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 MSU to be directed 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 portion of this project that involves a water quality monitoring study of the James River basin 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 supports the monitoring project entitled, "Suspended Sediment and Dissolved Solid Transport in the James River, SW Missouri". It involves a suspended sediment and dissolved solids transport study in the upper and middle James River basin that supports efforts to understand sources of pollutants in the basin and the degree of variation in concentrations of pollutants throughout the year due to runoff and seasonal influence. The goal is to adequately describe the dynamics of solids transport in karst-dominated Ozark watersheds which is vital for water quality management.

PROJECT AND TASK DESCRIPTION

Project Schedule and Time Line

Sampling sites were selected and personnel were trained to complete laboratory and field procedures from June 2008 to August 2008. See Table 2 for project schedule and time line.

The monitoring phase of this project will begin September 2008 and will end October 2009, spanning 13 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. 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 four events per month. All sites with flow during storm events will be sampled. See Table 3 for site identification, drainage area, and land use.

Water quality indicators that will be measured for water samples collected are listed in Table 4. All indicators will be collected during fixed-interval and storm-chasing sampling. Discharge data for each site will be retrieved from the United States Geological Survey (USGS) website using the time of water sample collection.

Data processing will involve the creation of concentration and load frequency relationships using the load-duration curve method (Crawford, 1996). 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 the dynamics of suspended sediment and dissolved solids transport in karst-dominated Ozark Watersheds to improve water quality management in the James River and lake arm areas. The final report will be completed by February 1, 2010.

Sampling Sites and Frequency

The sampling sites were selected based on the location of USGS continuous discharge gaging stations within the basin. Table 3 summarizes the sample sites selected for this project. The locations of sampling sites are shown in Figure 2. Water samples will be collected during fixed-interval and storm-chasing events and split to provide samples for the analysis of total suspended solids, total dissolved solids, total and dissolved organic and inorganic carbon, the anions of interest, total nitrogen, and total phosphorus. Temperature, pH, conductivity, dissolved oxygen, and turbidity data

will be gathered during fixed-interval and storm-chasing sampling. Discharge will be recorded from USGS gage stations during time of water sample collection. Table 4 summarizes the sampling techniques for all analytes of interest.

For quality control purposes, cross channel sampling will occur at one site per sampling event. Water samples will be collected at three locations along a cross section and analyzed individually to determine variation of water quality parameters within the channel. The channel will be divided into 3 sections along the cross section and sampling will occur in the center of each section as described in standard operating procedure "Indirect Method for Flow Discharge Estimation" (2080R01 Indirect Flow.doc). The site chosen for sampling in this manner will rotate among the sites throughout the project sampling period so that cross channel data are collected at each site. Relative standard deviation values of cross-channel triplicates will provide a statistical estimation of sampling error associated with both stormwater and baseflow sample collection at each site.

Work Schedule for Sample Collection and Analysis

Water samples for all analytes of interest and in-situ water parameter data will be collected during fixed-interval and storm-chasing sampling at all sites with flow.

Water samples will be collected using a depth-integrated sampler for the analysis of total suspended solids, total dissolved solids, total and dissolved organic and inorganic carbon, fluoride, chloride, bromide, nitrate, nitrite, sulfate, total nitrogen, and total phosphorus. Water samples will be collected in 500ml bottles, transported on ice, transferred to the laboratory with a chain of custody form, and analyzed prior to appropriate hold times for each analyte of interest. The 500ml will be split to provide samples for all of the analyses. Appendix B contains a flowchart illustrating sample distribution for analysis. Three hundred milliliters of each water sample will be filtered through a 1.5 μm nominal pore size glass microfiber filter and then filtered through a 0.45 μm nominal pore size glass microfiber filter. Filters will be used for total suspended solids determination. The filtrate will be split into 100ml for TDS determination, 100ml for dissolved organic and inorganic carbon determination, and 100ml for anion determination and stored at 4°C. The remaining 200ml of unfiltered water sample will be split into 100ml for total organic and inorganic carbon determination and 100ml for total nitrogen and total phosphorus determination. The 100ml for total organic and inorganic carbon analysis will be stored at 4°C. The 100ml split for nutrient analyses will be acidified within the original sample bottle and stored at 4°C for nutrient analyses. The data from all analyses will be processed by the OEWRI QA/QC coordinator, recorded in a spreadsheet, and 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.

Sites were selected in conjunction with USGS gaging stations so discharge data can be acquired for each site based on the time that each water sample is collected. Discharge data for each event will be retrieved upon return to the laboratory.

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.

Laboratory measured analytes:

1. Total Suspended Solids (TSS) (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.

2. Total Dissolved Solids (TDS) (SOP: TDSolids): Total dissolved solids, is a combination of all molecular, ionized, or colloidal sol forms of inorganic and organic substances that pass through a 1.5 μm filter and then a 0.45 μm filter. The USGS found that methods used for the analysis of wastewater are not always appropriate for the analysis of natural-water samples (USGS, 2000). Total suspended solid (TSS) concentrations are not comparable to suspended-sediment concentrations (SSC) when natural-water samples are analyzed and suggest that the SSC analytical method be used to enhance the accuracy and comparability of suspended solid-phase concentrations of natural waters. The primary difference between the TSS and SSC methods is the nominal pore size of the filter used to retain suspended materials. The TSS method uses a 1.5 μm filter and retains sand, silt, and coarse clay fractions in a water sample. A 0.45 μm nominal pore size filter retains the medium, fine, and very fine clay fractions in addition to the fractions that the 1.5 μm filter retains therefore those fractions are included in the final computation and give a more accurate quantification of suspended solid-phase concentrations of natural waters therefore. Calcium, phosphates, nitrates, sodium, potassium, and chloride are commonly found in stormwater runoff from sources such as agricultural operations and industrial or sewage treatment point sources. TDS is used as an aesthetic indicator of drinking water and as an aggregate indicator of a broad array of chemical contaminants. A known volume of sample filtrate is evaporated and mass differential calculations are used to determine the total dissolved solids in each sample.

3. Total Phosphorus (TP) (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.

4. Total Nitrogen (TN) (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.

5. Total and Dissolved Organic Carbon (NPOC) (SOP: TIC/TOC R01): Organic carbon is material derived from decaying vegetation, bacterial growth, metabolic activities of living organisms, and from synthetic sources such as detergents, pesticides, fertilizers, and industrial chemicals. Natural organic matter produces humic acid, amines, and urea. Organic carbon is a non-specific indicator of water quality. Total organic carbon is derived by analyzing samples that have not been filtered. Dissolved organic carbon is

what remains in the sample after the sample has been filtered using a 0.45 µm filter. A sparger purges volatiles from the samples, inorganic carbon is digested with hydrochloric acid, a high temperature catalytic oxidation occurs using a two-zone combustion reactor that separates the matrices and protects the catalyst, and carrier gas takes the gases through a three-step drying process and delivers them to the detector for measurement.

6. Total and Dissolved Inorganic Carbon (TIC/NPOC) (SOP: TIC/TOC R01): Inorganic carbon originates from naturally occurring ores and minerals and from synthetic sources such as detergents, pesticides, fertilizers, and industrial chemicals. Inorganic carbon is a non-specific indicator of water quality. Total inorganic carbon is derived by analyzing samples that have not been filtered. Dissolved inorganic carbon is what remains in the sample after the sample has been filtered using a 0.45 µm filter. A sparger purges volatiles from the samples, a high temperature catalytic oxidation occurs using a two-zone combustion reactor that separates the matrices and protects the catalyst, and carrier gas takes the gases through a three-step drying process and delivers them to the detector for measurement.

6. Fluoride (F⁻)(SOP: IC R01): Fluoride exists naturally in water sources and is derived from fluorine, the thirteenth most common element in the Earth's crust. Large municipalities often add fluoride to the water supply to bring the total fluoride concentration to approximately 1 ppm to aid dental health. Higher levels of fluoride found in surface water may indicate municipal leaks or industrial discharges. Water samples are injected into a stream of eluent and passed through a series of ion exchangers. Anions are separated and directed through a suppressor that converts the anions to highly conductive acid forms so that the anions can be measured by conductivity, identified based on retention time compared to standards, and quantified by peak height measurement.

7. Chloride (Cl⁻) (SOP: IC R01): Chloride originates in surface waters from natural sources. Anthropogenic sources include sewage and industrial effluent and urban stormwater runoff. Chloride concentration is used as an aesthetic indicator of water quality and can indicate point source pollution. Water samples are injected into a stream of eluent and passed through a series of ion exchangers. Anions are separated and directed through a suppressor that converts the anions to highly conductive acid forms so that the anions can be measured by conductivity, identified based on retention time compared to standards, and quantified by peak height measurement.

8. Bromide (Br⁻) (SOP: IC R01): Bromide can enter water from dissolution of a geologic source, from saltwater intrusion, and from industrial point sources. Bromide is a natural constituent of ground water and can be used as an indicator of the discharge of ground water to surface water. Brominated disinfection by-products can form during drinking water disinfection when bromide is present and these by-products are suspected carcinogens. Bromide concentrations can indicate water quality. Water

samples are injected into a stream of eluent and passed through a series of ion exchangers. Anions are separated and directed through a suppressor that converts the anions to highly conductive acid forms so that the anions can be measured by conductivity, identified based on retention time compared to standards, and quantified by peak height measurement.

9. Nitrate (NO_3^-) (SOP: IC R01): Nitrate sources are both organic and inorganic and include human sewage, livestock manure, and fertilizers. Stormwater runoff delivers nitrates to surface waters and septic tanks can affect groundwater. Excess nitrate concentrations in aquatic systems can lead to algae blooms and eutrophication. Nitrates are highly soluble, are a component of total dissolved solids, and are used as an indicator of water quality. Water samples are injected into a stream of eluent and passed through a series of ion exchangers. Anions are separated and directed through a suppressor that converts the anions to highly conductive acid forms so that the anions can be measured by conductivity, identified based on retention time compared to standards, and quantified by peak height measurement.

10. Nitrite (NO_2^-) (SOP: IC R01): Nitrite occurs naturally in water, soil, and plants. Anthropogenic sources include human sewage, livestock manure and fertilizers. Nitrite reacts directly with hemoglobin in warm-blooded animals to produce methemoglobin which destroys the ability of red blood cells to transport oxygen. Water samples are injected into a stream of eluent and passed through a series of ion exchangers. Anions are separated and directed through a suppressor that converts the anions to highly conductive acid forms so that the anions can be measured by conductivity, identified based on retention time compared to standards, and quantified by peak height measurement.

11. Phosphate (PO_4^{-3}) (SOP: IC R01): Phosphate occurs in living and decaying plant and animal remains, as free ions or weakly chemically bounded in aqueous systems, chemically bounded to sediments and soils, or as mineralized compounds in soil, rocks, and sediments. Anthropogenic sources include partially treated and untreated sewage, runoff from agricultural areas, and lawn fertilizers. Larger quantities of these compounds can be found in laundering and commercial cleaning fluids. 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. Water samples are injected into a stream of eluent and passed through a series of ion exchangers. Anions are separated and directed through a suppressor that converts the anions to highly conductive acid forms so that the anions can be measured by conductivity, identified based on retention time compared to standards, and quantified by peak height measurement.

12. Sulfate (SO_4^{-2}) (SOP: IC R01): Sulfate can naturally come from the decomposition of organic matter such as leaves, the dissolution of rock or soil containing gypsum, or from deposition from the atmosphere. Point sources include sewage treatment plants and

industrial discharges such as tanneries, pulp mills, and textile mills. Fertilizer contributes sulfates to stormwater runoff. Aquatic organisms utilize sulfur compounds and algae depend on sulfate for growth. Water samples are injected into a stream of eluent and passed through a series of ion exchangers. Anions are separated and directed through a suppressor that converts the anions to highly conductive acid forms so that the anions can be measured by conductivity, identified based on retention time compared to standards, and quantified by peak height measurement.

Quality Objectives and Criteria for Measurement Data

The objective of this project is to determine the dynamics of suspended sediment and dissolved solids transport in karst-dominated Ozark Watersheds to improve water quality management in the James River and lake arm areas. 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

Accuracy: 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).

Bias: 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).

Comparability: 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 OEWR for all water quality projects.

Completeness: 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.

Precision: 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).

Representativeness: 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 James River Watershed.

Sensitivity: 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: "James SS & DS". 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.

Quality Assurance Project Plan (QAPP): 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.

Standard Operating Procedures (SOPs): 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 A.

Chain of Custody forms: 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.

Field Notebooks: 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.

Laboratory Bench sheets: 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.

Quality Assurance documents: 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.

Final and Quarterly Progress reports: 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 determine the dynamics of suspended sediment and dissolved solids transport in karst-dominated Ozark Watersheds to improve water quality management in the James River and lake arm areas. The 5 sampling sites for the project were chosen based on accessibility, water volume in the channel, location in the basin, and proximity to USGS gage stations. Analytes include total suspended solids, total dissolved solids, total nitrogen, total phosphorus, total and dissolved organic and inorganic carbon, fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfate. 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.

Sampling Methods

Surface water samples for total suspended solids, total dissolved solids, nutrients and anions will be collected by the depth integrated sampling technique (SOP: 1040R01 Water Sampling.doc) using a US DH-48 wading type sampler and 500 ml plastic bottles from flowing water. Cross channel sampling will occur at one site per sampling event.

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 in the field. Each 500ml sample will be split to provide samples for the analysis of total suspended solids, total dissolved solids, total nitrogen, total phosphorus, total and dissolved organic and inorganic carbon, and anions of interest. Three hundred milliliters of each water sample will be filtered through a 1.5 μm nominal pore size glass microfiber filter and then filtered again through a 0.45 μm nominal pore size glass microfiber filter. The filtrate will be split into 100ml for TDS determination, 100ml for dissolved organic and inorganic carbon determination, and 100ml for anion determination and stored at 4°C. The remaining 200ml of water sample will be split to provide samples for the analysis of total nutrients and total organic and inorganic carbon. One 100ml split will be acidified within the original sample bottle and stored at 4°C for nutrient analyses. The other 100ml split will be transferred to a separate bottle and stored at 4°C for total organic and inorganic carbon analyses. 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.

All sites have a United States Geological Survey (USGS) gage already in place that provides real-time discharge data via the internet.

Sample Handling and Custody

See Table 6 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 James River field notebook.

Water samples are collected in appropriate bottles 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 re-analyzed 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.

Individual SOPs specifically present all equations used to determine quality control measures for each parameter associated with this project. Relative percent difference (RPD) will be calculated for pairs of duplicate analyses to determine precision. The coefficient of variation (CV%) will be used to determine precision if triplicates are required for specific parameters. Accuracy will be determined by calculating RPD between multiple analyses of manufacturer- or laboratory-certified standards throughout each batch of samples. The effectiveness of digestion procedures will be determined by calculating percent recovery of matrix spike solutions. The Method Detection Limit (MDL) for each type of chemical analysis is calculated by multiplying 3.14 and the standard deviation of multiple analyses of the blank associated with the analysis. The "3.14" value is derived from the table of a one-sided *t* distribution when a 99% confidence level is desired.

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 7 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.

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 8 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). Initial calibrations are recorded by the technician and included within the data set that is reviewed by the QA/QC coordinator.

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. Instrument performance checks are recorded by the technician and included within the data set that is reviewed by the QA/QC coordinator.

See Table 9 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. The QA/QC coordinator will receive and inspect supplies and consumables upon delivery and return them if they do not meet specifications.

Sample bottles used to collect samples and individual parameter bottles used to store splits of 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 water again. The bottles are allowed to drain dry and then are stored in sealed plastic bags until use. Bottles will routinely be 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.

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

Non-direct discharge measurements are required for this project. Those measurements will be taken from the USGS website for each site. Project assistants may want to obtain weather data from the National Weather Service to check rain totals as well.

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.

Field notebooks: The field notebook will be similar to item number 8152-55 manufactured by Sokkia and will be titled “James SS & DS”. 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 OEWR office.

Field Instrumentation: Data internally stored in the PDA associated with the Eureka Amphibian with Manta will be downloaded to the laboratory computer file titled “James SS & DS”. 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 James SS & DS NPS removable drive. All data printouts will be stored in the project file in the OEWR office.

Laboratory Instrumentation: Data internally stored on a computer associated with a laboratory instrument will be saved to the file titled “James SS & DS”. Raw instrument data will be stored in a James SS & DS 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 James SS & DS NPS removable drive. All data printouts will be stored in the project file in the OEWR 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 OEWR 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.

Readiness Review: 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.

Proficiency Testing: A sample with a known-concentration of analyte will be purchased from an appropriate vendor such as those referenced in appropriate SOPs. 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.

Surveillance Assessment: 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 by the project manager and submitted by the principal investigator. 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 OEWR office. Project management will forward information to outside agencies including USEPA oversight personnel associated with this project.

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.

Data Review: 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.

Data Verification: 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.

Data Validation: 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 determine the dynamics of suspended sediment and dissolved solids transport in karst-dominated Ozark Watersheds to improve water quality management in the James River and lake arm areas 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

Crawford, C.G., 1996. Estimating Mean Constituent Loads in Rivers by the Rating-Curve and Flow-Duration, Rating-Curve Methods. PhD dissertation, University of Bloomington, Bloomington, Indiana.

U.S. Geological Survey, Water-Resources Investigations Report 00-4191, 2000.

TABLES

Table 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 and QA 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 for field and laboratory procedures.	417-836-3198 hhoggard@MissouriState.edu	2
Marc Owen Research Specialist II	OEWRI	GIS Support.	417-836-3197 MOwen@MissouriState.edu	3
Derek Martin Research Specialist GIS Manager	OEWRI	Mapping.	417-836-3015 DJMartin@MissouriState.edu	4
Dr. Richard Biagioni, MSU Faculty	MSU Chemistry	Supervise chemistry analyses.	417-836-4649 RNBiagioni@MissouriState.edu	5
Regina Kidwell, USEPA Region 7 Administration, KC	United States Environmental Protection Agency	USEPA Oversight, KC	913-551-7788 kidwell.regina@epa.gov	6
Jaci Ferguson, USEPA Region 7 Administration, Springfield	United States Environmental Protection Agency	USEPA Oversight, Springfield	417-575-8028 ferguson.jaci@epa.gov	7
Diane Harris, USEPA QA Manager	United States Environmental Protection Agency	USEPA QA Oversight	913-551-7258 harris.dianee@epa.gov	8

Name and Title	Organization	Responsibilities	Contact Information	QAPP Receipt/ Control number
Erin Hutchison Graduate Assistant	MSU	Collect and analyze samples, record maintenance, reporting.	417-836-8705 Erin683@MissouriState.edu	9

Table 2. Project Schedule Time Line.

Activity	Date (MM/DD/YYYY)		Deliverable	Deliverable Due Date
	Anticipated Start Date	Anticipated Completion Date		
Select sampling sites	06/01/2008	06/13/2008	Approved sample site map	06/15/2008
Sample Collection and Laboratory Analysis Training	06/13/2008	08/31/2008	Memo	08/31/2008
Bi-Monthly Water Chemistry Sampling and Storm Chasing	09/30/2008	10/31/2009	Memo	10/31/2009
Data Processing	09/30/2008	10/31/2009	Memo	10/31/2009
Final Report/Publication	10/31/2009	01/31/2010	Report	02/1/2010

Table 3. Sample Site Summary

Site ID	Location	UTM Northing	UTM Easting	Drainage Area (km ²)	% High Den Urban	% Low Den Urban	% Barren	% Crops	% Grass	% Forest	% Water
J-K	James River at Kinser Bridge	4,111,529.732	481,982.022	637	1.9	2.8	1.1	7	51.8	34.7	0.7
W	Wilson Creek at Scenic Ave	4,115,662.167	470,591.075	46.1	40.4	46.8	0	0.3	8.1	4.2	0.2
J-SR	James River at Shelvin Rock	4,095,680.404	467,576.888	1,197	7	10.1	1	5	50.6	25.5	0.8
F	Finley River at Seneca Bridge	4,092,114.741	470,810.641	676	1.9	2.8	1.1	2.6	60.7	30.5	0.6
P	Pearson Creek at FR 148	4,114,633.632	482,384.734	54.4	53.4	4.7	12.4	0.6	5.5	61.2	15.2

Coordinate system = UTM NAD83 Zone 15

Table 4. Sampling Techniques

Sampling Device or Procedure	Collected By	Sites	Location	Number collected	Analytes
Depth-integrated Sample	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Total Suspended Solids
Depth-integrated Sample	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Total Dissolved Solids
Depth-integrated Sample	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Nutrients (total phosphorus, total nitrogen)

Depth-integrated Sample	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Total and Dissolved Organic and Inorganic Carbon
Depth-integrated Sample	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Anions (fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfate)
<i>In situ</i> , multi-probe	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Temperature
<i>In situ</i> , multi-probe	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	pH
<i>In situ</i> , multi-probe	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Specific Conductivity
<i>In situ</i> , multi-probe	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Dissolved Oxygen
<i>In situ</i> , multi-probe	Project Assistant	All Sites	Stream	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Turbidity
Internet, database	Project Assistant	All Sites	http://waterdata.usgs.gov/mo/nwis/sw	Fixed-Interval = 2 per month Storm-chasing = up to 4 per month	Discharge

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
Total Suspended Solids	TSSolids	Accuracy	± 20%	LB
		Bias	± 20%	LB
		Precision	± 20% RPD	LD
		Sensitivity	≤ 0.5 mg/L	MDL, LRB
Total Dissolved Solids	TDSolids	Accuracy	± 20%	LB
		Bias	± 20%	LB
		Precision	± 20% RPD	LD
		Sensitivity	≤ 0.1 mg/L	MDL, LRB
Total Nitrogen	3020R01 TotalIN	Accuracy	± 20%	LB, LS
		Bias	± 20%	LB, LS
		Precision	± 20% RPD	LD
		Sensitivity	≤ 0.1 mgN/L	MDL, LRB
Total Phosphorus	3010R01 TotalIP	Accuracy	± 20%	LB, LS
		Bias	± 20%	LB, LS
		Precision	± 20% RPD	LD

Matrix = Water		Sampling Procedure = Grab Sample		
Parameter	SOP	Data Quality Indicator	Measurement Performance Criteria	QC Sample Type to assess Measurement Performance
		Sensitivity	≤ 0.005 mgP/L	MDL, LRB
Total and Dissolved Organic and Inorganic Carbon	TICTOC-R01	Accuracy	± 20%	LB, LS
		Bias	± 20%	LB, LS
		Precision	± 20% RPD	LD
		Sensitivity	≤0.5 mg/L for all forms	MDL, LRB
All Anions	IC R01	Accuracy	± 20%	LB
		Bias	± 20%	LB
		Precision	± 20% RPD	LD
		Sensitivity	currently under review (September 2008)	MDL, LRB
pH	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	0° C	Ice bath
Conductivity	Eureka Snapshot	Accuracy	± 20%	LB, LS
		Bias	NA	ND

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

*LB = Laboratory Blank (reference sample), LS = 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

Table 6. Sample Collection Conditions for Analytes.

Analyte	Bottle Type	Bottle Size	Preservative	Holding time	SOP Reference
Total Suspended Solids	Plastic	500 ml	<4°C	7 days	TSSolids
Total Dissolved Solids	Plastic	500 ml	<4°C	7 days	TDSolids
Total Nitrogen	Plastic	500 ml	H ₂ SO ₄ to pH ≤ 2 Ice	28 days	3020R01 TotalN
Total Phosphorus	Plastic	500 ml	H ₂ SO ₄ to pH ≤ 2 Ice	28 days	3010R01 TotalP
Total and Dissolved Organic and Inorganic Carbon	Plastic	500 ml	<4°C	48 hours	TIC/TOC R01
Anions	Plastic	500 ml	<4°C	48 hours	IC R01
Field Parameters	These parameters are collected <i>in situ</i> .				
pH	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

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

QC Type and Error	Corrective Action	Comment*
Laboratory Reagent Blank > MDL	<ol style="list-style-type: none"> 1. Analyze another blank; if 2nd LRB is acceptable, then data is acceptable. 2. 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	<ol style="list-style-type: none"> 1. If Reference sample (LS) is acceptable, then qualify the data 2. 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	<ol style="list-style-type: none"> 1. Analyze another LB. 2. If 2nd LB fails then check another source for the reference material. 3. 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	<ol style="list-style-type: none"> 1. Check calculations for error, correct if found 	No comment needed for corrected calculations.
Calibration Standards fail	<ol style="list-style-type: none"> 1. Check calibration standards against the reference sample. 2. 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		

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

Equipment / Instrument	Maintenance, Testing, or Inspection Activity	Frequency	SOP Reference
Sampling Equipment			
Eureka	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 Equipment			
Spectrophotometer	Create calibration curve	For each use	3010R01 Total P
Spectrophotometer	Create calibration curve	For each use	3020R01 Total N
IC	Create calibration curve	For each use, for each anion	IC R01
TIC/TOC	Create calibration curve	For each use, for each form	TIC/TOC R01

Table 9. Instrumentation Requiring Calibration.

Instrument	Analyte	Calibration Type	SOP Reference
Eureka	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
IC	Fluoride, Chloride, Nitrite, Bromide, Nitrate, Phosphate, Sulfate	Calibration Curve	IC R01
TIC/TOC	Organic and Inorganic Carbon (Total and Dissolved)	Calibration Curve	IC R01

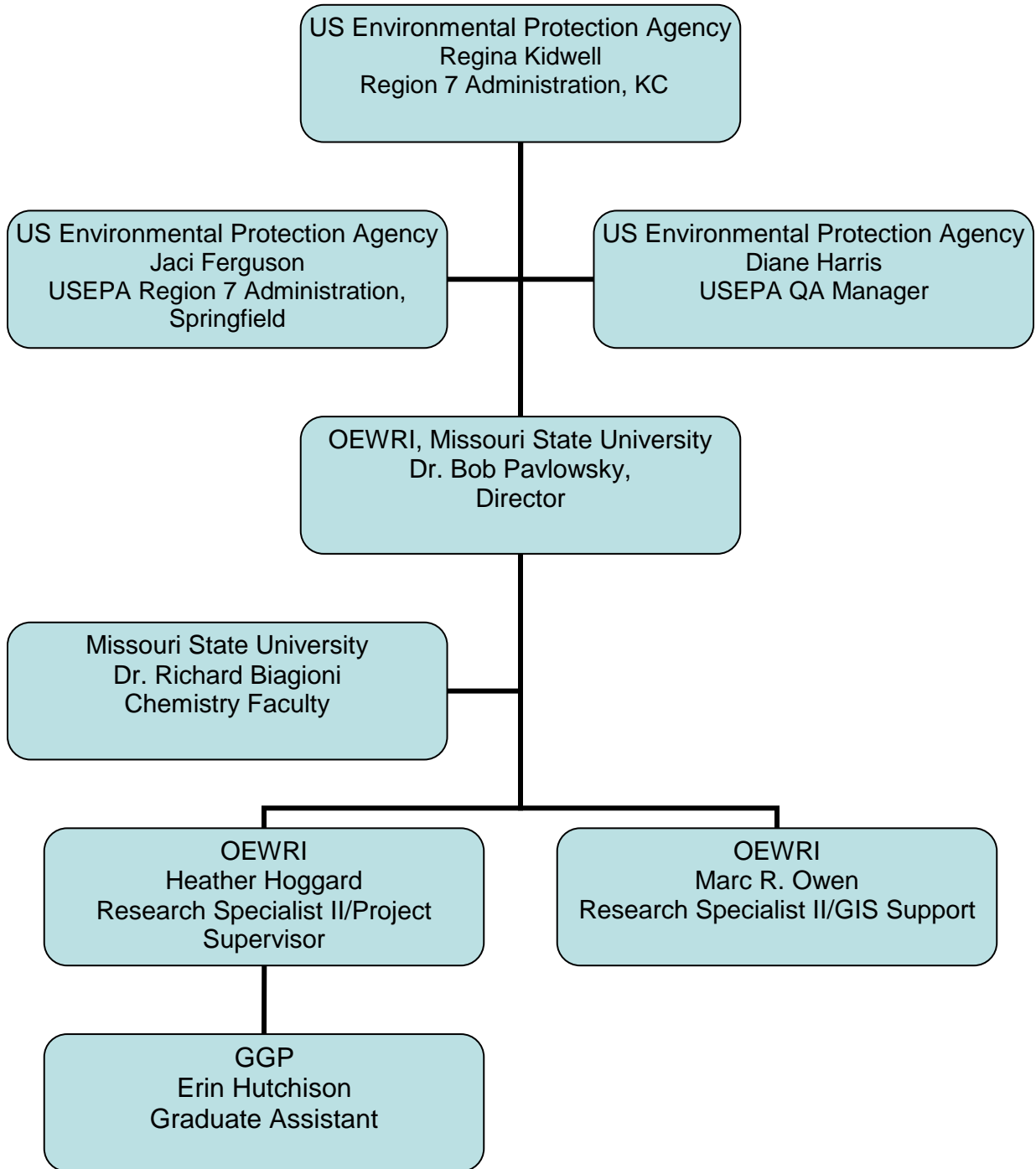


Figure 1. Organizational chart showing lines of authority and reporting responsibilities.

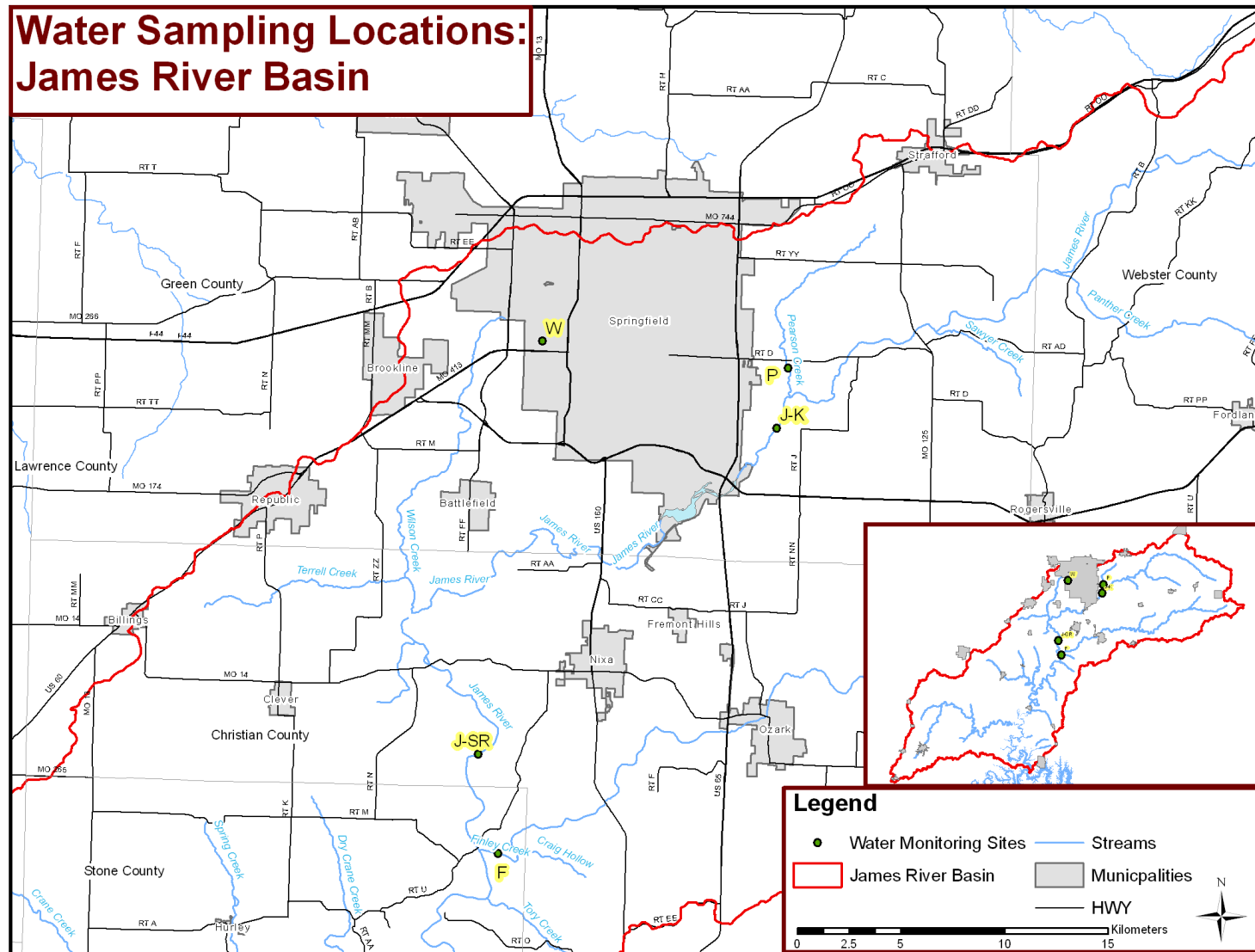


Figure 2. James River Basin and Sampling Sites.

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
TSSolids	Total Suspended Solids	Final
TDSolids	Total Dissolved Solids	Final
TIC/TOC R01	Total and Dissolved Organic and Inorganic Carbon	Final
IC R01	Anions	Under Review
0150R01 Bottle Prep non-Metals	Preparation of Sample Bottles For non-Metal Analyses	Final

APPENDIX B. Flowchart of Sample Distribution for Analyses.

