

**Appendix A:  
Quality-Assurance Plan**

**Expanded Groundwater Monitoring for Nonpoint-Source Pollution  
Assessment in the Jackson Purchase Region of Kentucky,  
Bounded by the Tennessee, Ohio, and Mississippi Rivers  
(Basin Management Unit 3)**

**Prepared by  
Water Resources Section  
Kentucky Geological Survey  
University of Kentucky**

## Organizations Implementing Project

Kentucky Geological Survey, University of Kentucky  
Kentucky Division of Water

### Effective Date

June 2004–November 2007

### Approving Officials

Kentucky Geological Survey QA Officer: \_\_\_\_\_

Kentucky Geological Survey Principal Investigator: \_\_\_\_\_

Kentucky Division of Water Representative: \_\_\_\_\_

## Project Management Elements

### A3—Distribution List

Glynn Beck, Kentucky Geological Survey  
Peter Goodmann, Manager, Division of Water–Groundwater Branch  
Jack Moody, Acting Quality Assurance Officer, Division of Water

### A4—Project/Task Organization

**Key Personnel.** Research staff of the Kentucky Geological Survey (KGS), University of Kentucky, will coordinate this project in cooperation with staff of the Groundwater Branch, Kentucky Division of Water.

KGS research staff, in cooperation with the Groundwater Branch, Kentucky Division of Water, will scout and select 60 suitable sampling locations. KGS staff will perform sampling and sample delivery. The Groundwater Branch, Kentucky Division of Water, may assist KGS personnel with sample delivery. The Kentucky Department for Environmental Protection's Division of Environmental Services Laboratory will be responsible for sample analysis. All data generated will be delivered to the Kentucky Department for Environmental Protection's Consolidated Groundwater Database and will be forwarded to the Kentucky Geological Survey's Groundwater Data Repository.

R. Stephen Fisher will be the principal investigator and QA officer. Address: Kentucky Geological Survey, 228 MMRB, University of Kentucky, Lexington, Kentucky 40506-0107. Phone (859) 257-5500.

E. Glynn Beck will be the project officer and field sampling officer. Address: Kentucky Geological Survey, Western Kentucky Office, 1401 Corporate Court, Henderson, Kentucky 42420. Phone (270) 827-3414.

#### Laboratory

Division of Environmental Services  
100 Sower Boulevard  
Frankfort, Kentucky 40601  
(502) 564-6120

**Participating Agencies.** The Groundwater Branch, Kentucky Division of Water, currently conducts statewide groundwater monitoring for the Ambient Groundwater Monitoring Program. The Kentucky Geological Survey performs groundwater research but is not currently conducting other monitoring activities.

### A5—Problem Definition/Background

Previous work (Conrad and others, 1999; Kentucky Division of Water, 2000; Beck and others, 2004) and the experience of Division of Water staff show that many shallow wells in the Jackson Purchase Region produce groundwater that contains high nitrate concentrations and smaller but significant amounts of other nonpoint-source (NPS) chemicals. Identifying the sources of the NPS contaminants is important because groundwater is used extensively for both domestic and public water supplies in the area and will continue to be an important source of drinking water for the foreseeable future, and because groundwater recharges the surface-water resources.

## **A6—Project/Task Description**

The Kentucky Division of Water currently conducts quarterly nonpoint-source groundwater monitoring at approximately 70 sites across the state. This project will expand that monitoring effort in the Jackson Purchase Region (JPR), which is bounded by the Tennessee, Ohio, and Mississippi Rivers (Kentucky Basin Management Unit 3), by increasing the number of monitoring sites and focusing additional efforts of the existing monitoring network in these watersheds.

The goal of this project is to identify the impacts of nonpoint-source pollution on the groundwater in basins of the lower Tennessee River and tributaries of the Ohio and Mississippi Rivers. The objective of this study is to identify aquifers that have been impacted by nonpoint-source pollution. Problems in these areas will be identified in order that future nonpoint-source resources may be properly focused regarding nonpoint-source pollution prevention and pollution abatement.

**Study Area Description.** The Tennessee River Basin drains the Mississippi Plateaus and Mississippi Embayment physiographic provinces. However, only wells located in the Mississippi Embayment physiographic province will be sampled for this project.

In the Mississippi Embayment (Jackson Purchase), shallow sand and gravel deposits provide abundant good-quality water to wells. Approximately 43,600 residents are served by 19,500 private wells. Public groundwater supplies provide water for an additional 108,000 people.

Tributaries of the Mississippi River drain the Mississippi Embayment physiographic province (described above).

The minor Ohio River tributaries included in Basin Management Unit 3 primarily drain the thick alluvium along this major river in the Mississippi Embayment physiographic province (described above).

### **Watershed Information**

*Stream Names.* Lower Tennessee River and tributaries of the Ohio and Mississippi Rivers.

*Major River Basins.* Basins of the lower Tennessee River and tributaries of the Ohio and Mississippi Rivers.

### **USGS Hydrologic Unit Number**

Lower Tennessee River Basin:	06040005
	06040006
Mississippi River Basin:	08010100
	08010201
	08010202
Minor Ohio River Tributaries:	05140206

**Stream Order.** This project encompasses basins of the lower Tennessee River and tributaries of the Ohio and Mississippi Rivers.

### **Counties in the Study Area**

*Lower Tennessee River Basin:* Calloway, Graves, Marshall

*Tributaries of the Mississippi River:* Ballard, Calloway, Carlisle, Fulton, Graves, Hickman, McCracken

*Tributaries of the Ohio River:* Ballard, McCracken

## **A7—Quality Objectives and Criteria**

Groundwater-quality data collected from this project will be utilized to complete the following objectives.

- (1) Determine impacts of nonpoint-source pollution on groundwater resources in selected areas of basins of the lower Tennessee River and tributaries of the Ohio and Mississippi Rivers.
- (2) Provide guidance for the nonpoint-source program to focus future resources relating to nonpoint-source pollution of groundwater.
- (3) Support other programs, such as the Wellhead Protection Program, the Groundwater Protection Plan Program, and the Agriculture Water Quality Authority.
- (4) Provide additional data useful for the long-term management of the resource.

## **A8—Special Training/Certification**

This section is not applicable because no special training or certification will be required to complete this project in its entirety.

## **A9—Documents and Records**

All chain-of-custody and lab reports will be maintained in the Groundwater Branch for the required document-retention period for the grant. At the end of the required period, documents will be archived by the Groundwater Branch Data Management and Support Section and stored in electronic format in the Kentucky Department for Environmental Protection's Consolidated Groundwater Database and the Kentucky Geological Survey's Groundwater Data Repository.

## **Data Generation and Acquisition Elements**

### **B1—Sampling Process Design**

**Monitoring Approaches.** Monitoring of approximately 60 sites will begin in late March or April 2005, depending on weather and application of agricultural chemicals. Specific sample sites will be selected after the Division of Water's groundwater database has been reviewed for candidate sites and field inspection has confirmed that the candidate sites are suitable for monitoring. For all selected sites, a "Kentucky Water Well Record" (example attached) will be placed on record with the Division of Water. Duplicate samples will be collected for at least 10 percent of all samples in order to check reproducibility and provide QA/QC.

Field reconnaissance will be conducted prior to final site selection to assess the suitability and accessibility of each site. The appropriate well-inspection record will be completed. Site locations will be plotted on 7.5-minute topographic maps and identified by a site name and unique identification number (AKGWA number) for incorporation into the Department for Environmental Protection's Consolidated Groundwater Data Base and the Kentucky Geological Survey's Groundwater Data Repository.

**Monitoring-Station Location Strategy.** Monitoring-station locations may include stations that have been previously sampled by Kentucky Geological Survey personnel and stations that have not been previously sampled in the basin. All monitoring sites will be water wells.

**Sample Frequency and Duration.** The first round of sampling will encompass 60 water wells, which will be sampled in late March or April and May 2005. The same 60 water wells will be sampled in September and October 2005.

**Sample Parameters, Containerization, Preservation, and Handling.** Consistent with other monitoring efforts, samples will be collected at each well and analyzed for some or all of the following: major inorganic ions; nutrients; total organic carbon; caffeine; pesticides, including the most commonly used herbicides, insecticides, and fungicides; dissolved and total metals; and bacteria (total coliform and fecal coliform). The analytical methods, containers, volumes collected, preservation, and sample transport will be consistent with the Division of Water's "Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects," prepared by the Water Quality Branch (August 1995). Parameters to be measured, volume required for analysis, container type, preservative (if any), holding times (if any), and analytical methods are shown on the attached chain-of-custody form.

Major inorganic ions are used to establish background groundwater chemistry and also used to measure impacts from nonpoint-source pollutants such as abandoned mine lands and abandoned oil and gas production operations by measuring pH, alkalinity, chloride, sulfate, and fluoride. Nutrients and total organic carbon are used to measure impacts from agricultural operations (ammonia, nitrate, nitrite, TKN, and orthophosphate) and/or improper sewage disposal (nitrates, ammonia). Caffeine will be analyzed to better determine the impact of improper sewage disposal on groundwater. Pesticides are measured to determine both rural agriculture and urban domestic and commercial-use impacts on groundwater. Metals are used to establish the rock-groundwater chemistry and establish local and regional backgrounds for metals.

All samples will be analyzed by the Division of Environmental Services Laboratory according to the appropriate EPA method.

Bacteria will be sampled by Groundwater Branch, Kentucky Division of Water, personnel. Because of logistic considerations, a mobile bacteria lab will be used to analyze water-well samples on site for total coliform and fecal

coliform. On-site analysis will ensure that bacteria samples are analyzed within the required holding times (6 hr for fecal coliform, 24 hr for total coliform). A minimum of 40 water wells will be sampled twice for bacteria. After the initial sample, well owners will be asked to shock-chlorinate those wells that contain total coliform and/or fecal coliform. After a designated time period, each well will be sampled again for bacteria by Groundwater Branch, Kentucky Division of Water, personnel.

## **B2—Sampling Methods**

Before sampling begins, each well will be purged three well volumes or until pH, conductivity, and temperature have equilibrated. Samples will be collected from the most accessible location (outside faucet, kitchen faucet, etc.). Samples will be collected from the same location during both sampling events.

Whenever possible, sample collection is conducted using the sample container, except for dissolved metals, which is filtered on-site using a Teflon bucket and peristaltic pump. At each site, water from the Teflon bucket will be pumped through new (unused) tubing and a new 0.45-micron filter into the sample container.

## **B3—Sample Handling and Custody**

Sample containers will be labeled with the site name and well identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. Sampling personnel will complete a chain-of-custody record, developed in conjunction with the DES laboratory, for each sample. The DES laboratory will be responsible for following approved laboratory QA/QC procedures, conducting analyses within the designated holding times, following EPA-approved analytical techniques, and reporting analytical results to the Groundwater Branch.

A sample chain-of-custody form is attached.

## **B4—Analytical Methods**

All analytical methods, with the exception of field parameters (pH, temperature, and conductivity), will be performed by the Division of Environmental Services laboratory according to the appropriate EPA method. Field parameters will be determined according to the field meters manufacturer's instructions.

## **B5—Quality Control**

**Decontamination Protocols.** All sampling supplies that come in contact with the sample will be new, disposable equipment, or will be decontaminated prior to and after each use, using the following protocols.

**Sample Collection and Filtration Equipment.** Whenever possible, sample collection is conducted using the sample container, except for dissolved metals, which is filter on-site. Sample-collection equipment such as bailers and buckets will consist of Teflon. Pesticide samples will be collected using the sample container or a stainless-steel bailer or bucket, in order to avoid the problem of pesticide adsorption to the sampling device (as is considered to occur with Teflon instruments). Any reusable equipment will be decontaminated by rinsing with a 10 percent hydrochloric acid (HCl) solution, triple-rinsed with deionized water, and triple-rinsed with water from the source to be sampled prior to collecting a sample. After sampling is complete, excess sample will be disposed of, and the equipment will again be rinsed with the 10 percent HCl solution and triple-rinsed with deionized water.

New 0.45-micron filters will be used at each sampling site. Any tubing that contacts the sample will also be new. Any reusable-filter apparatus will be decontaminated in the same manner as sample-collection equipment. In addition, any intermediary collection vessel will be triple-rinsed with filtrate prior to use.

**Field Meters.** Field-meter probes will be rinsed with deionized water prior to and after each use.

**Equipment Calibration.** Field meters will be calibrated in accordance with the manufacturer's instructions.

**Sample Collection and Preservation/Contamination Prevention.** Water samples will be fresh groundwater collected prior to any type of water treatment. Samples not requiring field filtration will be collected directly in the sampling container. Samples requiring field filtration will be collected in a Teflon bucket decontaminated in accordance with decontamination protocols for sample collection and filtration equipment, filtered, and transferred to the appropriate container. Pesticide samples will be collected using the sample container or a stainless-steel bailer or bucket, wherever necessary.

Sample containers will be obtained from approved vendors, and will be new or laboratory-decontaminated in accordance with Division of Environmental Services accepted procedures. Sample containerization, preservation, and holding-time requirements are outlined in the Division of Water's "Standard Operating Procedures for Non-point Source Surface Water Quality Monitoring Projects," prepared by the Water Quality Branch (August 1995). Necessary preservatives will be added in the field; preservatives for dissolved constituents will be added after field filtration. Samples will be stored in coolers packed with ice for transport to the Division of Environmental Services laboratory.

Sample containers will be labeled with the site name and identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. Sampling personnel will complete a chain-of-custody record for each sample. The Division of Environmental Services laboratory will be responsible for following approved laboratory QA/QC procedures, conducting analyses within the designated holding times, following EPA-approved analytical techniques, and reporting analytical results to the Groundwater Branch.

Wells will be purged until conductivity readings stabilize prior to sampling, in order to ensure that groundwater, rather than water that has been standing in the wellbore, is being sampled.

**Duplicates and Blanks.** In order to check reproducibility and provide QA/QC control, one duplicate sample will be submitted with each batch of samples, regardless of the number of samples in the batch. One blank of deionized water (volatile trip blank) will be submitted for each sampling day. Deionized water used for the volatile trip blanks will be obtained from the Division of Environmental Services. Any significant deviations from duplicate samples will be flagged by Division of Environmental Services and those sites will be resampled or an explanation of the reason for the deviation will be given.

**Field Measurements.** Conductivity, temperature, and pH will be measured in the field at each site using portable automatic temperature compensating meters, and recorded in a field log book. Meters will be calibrated according to the manufacturer's specifications, using standard buffer solutions. Meter probes will be decontaminated according to decontamination protocols for field meters and stored according to the manufacturer's recommendations.

### ***B6—Instrument/Equipment Testing, Inspection, and Maintenance***

Division of Environmental Services laboratory personnel will carry out and follow in-house guidelines to ensure that all analytical equipment used is tested and working properly.

### ***B7—Instrument/Equipment Calibration and Frequency***

Division of Environmental Services laboratory personnel will carry out and follow in-house guidelines to ensure that all analytical equipment used is calibrated to maintain performance within specified limits.

### ***B8—Inspection/Acceptance of Supplies and Consumables***

E. Glynn Beck will be responsible for selecting and ordering all consumable supplies (sample bottles, tubing, filters, etc.). Sample containers will be obtained from approved vendors and will be new or laboratory-decontaminated in accordance with Division of Environmental Services accepted procedures. Deionized water used for blanks and rinsing sampling equipment will be obtained from the Division of Environmental Services.

### ***B9—Nondirect Measurements***

Data from the Kentucky Groundwater Data Repository will be accessed to identify possible water wells to be sampled in this project. The limitations of using these data are as follows:

- (1) The information listed in the database may not be accurate due to the historical nature of the data (well owners change, addresses change, etc.).
- (2) Each site will need to be field-checked to ensure the accessibility of the well and the accuracy of the data in the database.

### ***B10—Data Management***

In the field, sample containers will be labeled with the site name and well identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. In the office, sampling personnel will complete a chain-of-custody record, developed in conjunction with the DES laboratory, for each sample. In the laboratory, the DES laboratory will be responsible for following approved laboratory QA/QC procedures, conducting analyses within the designated holding times, following EPA-approved analytical techniques, and reporting

analytical results to the Groundwater Branch. Groundwater Branch and Kentucky Geological Survey personnel will enter the data into the Department for Environmental Protection's Consolidated Groundwater Data Base and the Kentucky Groundwater Data Repository, respectively.

See the attached forms,<sup>1</sup> which will be used throughout the data management process.

- (1) Field data sheet
- (2) Well and land-use background questionnaire
- (3) Water-well inspection form
- (4) Chain-of-custody form

## **Assessment and Oversight Elements**

### ***C1—Assessments and Response Actions***

The Nonpoint Source Section, and/or a Division of Water quality assurance officer (QAQ) may review all field and laboratory activities as requested. Any problems identified will be corrected based on recommendations by the QAO. KGS will notify the Division of Water of any known or suspected problems encountered during sampling activities.

### ***C2—Reports to Management***

KGS, in cooperation with DOW, will prepare a final report describing all methods and findings of the project. The final report will satisfy final report requirements for the grant.

## **Data Validation and Usability Elements**

### ***D1—Data Review, Verification, and Validation***

Groundwater Branch personnel will review all data for completeness and accuracy. Decisions to reject or qualify data will be made by Groundwater Branch hydrogeologists. KGS will notify the Division of Water of any known or suspected problems encountered during sampling activities.

### ***D2—Verification and Validation Methods***

Groundwater Branch hydrogeologists will investigate any unusual data. KGS will notify the Division of Water of any known or suspected problems encountered during sampling activities.

### ***D3—Reconciliation with User Requirements***

As soon as possible, data will be reviewed by both KGS and DOW and corrective action will be taken, if necessary. The cause of failure will be evaluated and corrected.

## **References Cited**

- Beck, E.G., Dinger, J., McMeans, M., Thom, W., and Henken, K., 2004, Status report: Bacteria and other contaminants in domestic water wells in the Jackson Purchase Region: University of Kentucky Cooperative Extension Service, Environmental and Natural Resources Issues Report ENRI-221, 6 p.
- Conrad, P.G., Carey, D.I., Webb, J.S., Dinger, J.S., and McCourt, M.J., 1999, Ground-water quality in Kentucky: Nitrate-nitrogen: Kentucky Geological Survey, ser. 11, Information Circular 60, 4 p.
- Kentucky Division of Water, 1995, Standard operating procedures for nonpoint source surface water quality monitoring projects: Kentucky Natural Resources and Environmental Protection Cabinet, 138 p.
- Kentucky Division of Water, 2000, Cumberland River Basin and Four Rivers Region status report: Kentucky Division of Water, 22 p.

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<sup>1</sup>Only the chain-of-custody form is appended to this report, in contrast to the original "Quality-Assurance Project Plan" prepared for the project.

**CHAIN OF CUSTODY RECORD**  
**NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET**  
**DIVISION OF WATER - GROUNDWATER BRANCH - 319 Project - Billing Code - ADD CODE**

<b>Site Identification</b>	<b>Collection Date/Time</b>	<b>Field Measurements</b>
Location: _____	Date: _____	Temp: _____ °C    pH: _____
County: _____	Time: _____	Cond: _____ mS/cm
AKGWA #: _____		Spring flow: _____

Sampler ID: \_\_\_\_\_

Division for Environmental Services Samples			
Analysis Requested	Container Size, Type	Preservation Method	Parameters
A	1000 ml Plastic Cubitainer	Cool to 4°C	<b>Bulk Parameters</b> Alkalinity, Chloride, Conductivity, Fluoride, Nitrate-N, Nitrite-N, pH, Sulfate, Total P, TSS, TDS, Ortho-P
B	1000 ml Plastic Cubitainer	H <sub>2</sub> SO <sub>4</sub> Cool to 4°C	<b>NH<sub>3</sub> / TKN / TOC</b>
C	1000 ml Plastic Boston Round	Filtered HNO <sub>3</sub> Cool to 4°C	<b>Dissolved Metals by ICP</b> Plus: Arsenic, Lead, Mercury, Selenium
D	1000 ml Plastic Boston Round	HNO <sub>3</sub> Cool to 4°C	<b>Total Metals by ICP</b> plus Arsenic, Lead, Mercury, Selenium
E	1000 ml Amber Glass	Cool to 4°C	<b>NP Pesticides</b> <b>Pesticides/PCBs</b> Methods 507/508
F	1000 ml Amber Glass	Cool to 4°C 50% HCl	<b>Herbicides/Caffeine</b> Method 555
	Two - 1000 ml Amber Glass	Cool to 4°C	<b>Duplicate</b> (only collect if requested)
G	Three 40ml Amber Glass	50% HCl (3-4 drops) Cool to 4°C No headspace	<b>VOCs</b> (Trip Blank Required)

**Signatures:**

Relinquished by: \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Received by: \_\_\_\_\_

Relinquished by: \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Received by: \_\_\_\_\_

Relinquished by: \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Received by: \_\_\_\_\_

Sample #: \_\_\_\_\_ Report #: \_\_\_\_\_

**DISCARD SAMPLES UPON COMPLETION**