Appendix A:
QA/QC Plan for Expanded Groundwater Monitoring for Nonpoint-Source Pollution Assessment in Basins of the Upper and Lower Cumberland River, Lower Tennessee River, and Tributaries of the Ohio and Mississippi Rivers (Basin Management Unit 3)

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1. Title Section

A. Project Name

Expanded Groundwater Monitoring for Nonpoint-Source Pollution Assessment in Basins of the Upper and Lower Cumberland River, Lower Tennessee River, and Tributaries of the Ohio and Mississippi Rivers (Basin Management Unit 3).

B. QA/QC Plan Preparers

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C. Date

March 13, 2000

D. Project 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 basins of the upper and lower Cumberland River, lower Tennessee River, and tributaries of the

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. This project is intended to work in coordination with other members of the River Basin Team who are conducting surface-water and biological sampling.

The goal of this project is to identify the impacts of nonpoint-source pollution on the groundwater in basins of the upper and lower Cumberland River, 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.

2. Project Organization and Responsibility

A. Key Personnel

Research staff of the Kentucky Geological Survey, 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 suitable sampling locations. KGS staff will perform sampling and 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 Kentucky Groundwater Data Repository.

Dr. R. Stephen Fisher will be the Project Officer, QA Officer, and Field Sampling Officer. Address: 228 Mining and Mineral Resources Building, University of Kentucky, Lexington, KY 40506-0107. Phone (859) 257-5500.

B. Laboratory

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

C. Participating Agencies

The Groundwater Branch, 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.

This project will cooperate with the Division of Water's Watershed Initiative; the upper and lower Cumberland, lower Tennessee, and Mississippi River Basin Teams; and the Division of Water's Water Quality Branch.

3. Watershed Information

A. Stream Names

Upper Cumberland River, lower Cumberland River, lower Tennessee River, and tributaries of the Ohio and Mississippi Rivers.

B. Major River Basins

Basins of the upper and lower Cumberland River, lower Tennessee River, and tributaries of the Ohio and Mississippi Rivers.

	USGS Hydrologic Unit Number
Upper Cumberland River Basin	05130101
	05130102
	05130103
	05130104
	05130105
Lower Cumberland River Basin:	05130205
	05130206
Lower Tennessee River Basin:	06040005
	06040006
Mississippi River Basin:	08010100
	08010201
	08010202
Minor Ohio River Tributaries:	05140206

C. Stream Order

This project encompasses basins of the upper and lower Cumberland River, lower Tennessee River, and tributaries of the Ohio and Mississippi Rivers.

D. Counties in the Study Area

Upper Cumberland River Basin: Adair, Bell, Casey, Clinton, Cumberland, Harlan, Jackson, Knox, Laurel, Letcher, Lincoln, McCreary, Metcalfe, Monroe, Pulaski, Rockcastle, Russell, Wayne, and Whitley.

Lower Cumberland River Basin: Caldwell, Christian, Crittenden, Livingston, Logan, Lyon, Simpson, Todd, and Trigg.

Lower Tennessee River Basin: Calloway, Graves, Livingston, and Marshall.

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

Tributaries of the Ohio River: Ballard and McCracken.

4. Monitoring Objectives

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

5. Study Area Description

The upper Cumberland River has headwaters in the Eastern Kentucky Coal Field physiographic province and flows into the eastern Mississippian Plateaus province.

The Eastern Kentucky Coal Field consists of relatively flat-lying, repetitive sequences of sandstone, shale, coal, and underclay, with minor amounts of limestone. These strata are highly dissected by streams, resulting in topographic relief of 300 to 3,000 ft between ridgetops and valley bottoms. According to 1990 U.S. Census data, approximately 280,000 people are served by private domestic wells, with an additional 50,000 people obtaining water from high-yield wells or springs. Most domestic wells are completed in fractured bedrock at depths less than 100 ft.

The Mississippian Plateaus (Pennyroyal) Region consists primarily of limestone strata with minor shales and siltstones, fractured sandstone, and unconsolidated alluvium along major rivers.

Limestone in this region is characterized by solution-enlarged sinkholes, caves, and caverns. Karst springs are the most common sources of groundwater, although shallow (less than 150 ft) wells in alluvium or fractured bedrock also provide water to some residents. Census data show that approximately 105,000 people are served by 45,000 private wells. An additional 180,000 people use groundwater from high-yield springs or wells.

The lower Cumberland River flows northward through the Mississippian Plateaus physiographic province (described above).

The Tennessee River Basin drains the Mississippian Plateaus and Mississippi Embayment physiographic provinces. The Mississippian Plateaus Region has been described above. 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).

6. Monitoring Program/Technical Design

A. Monitoring Approaches

Monitoring of approximately 30 sites will begin in April 2000. 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, either a *Kentucky Water Well Record* or a *Kentucky Spring Inventory Form* 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 or Spring Inventory records 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 Kentucky Groundwater Data Repository.

B. Monitoring Station Location Strategy

All monitoring station locations will be in addition to other stations currently sampled in the basin. All monitoring sites will be karst groundwater basin springs or karst windows, fracture springs, contact springs, or water wells.

C. Sample Frequency and Duration

Monitoring will begin in April 2000, and samples will be collected quarterly through March 2001.

D. Sample Parameters, Containerization, Preservation, and Handling

Consistent with other monitoring efforts, samples will be collected at each spring or well and analyzed for some or all of the following: major inorganic ions; nutrients; total organic carbon; pesticides, including the most commonly used herbicides, insecticides, and fungicides; and dissolved and total metals. 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 (total Kjeldahl nitrogen), and orthophosphate) and/or improper sewage disposal (nitrates, ammonia). Where sewage is suspected as a nonpoint-source pollutant, unbleached cotton fabric swatches may be used to detect optical brighteners, the whitening agents used in laundry products and commonly found in sewage (Quinlan, 1987). Pesticides are measured to determine both rural agricultural and urban domestic- and commercial-use impacts on groundwater. Metals are used to establish the rock-groundwater chemistry, establish local and regional backgrounds for metals, and determine nonpoint-source impacts from abandoned coal mine operations.

Bacteria will not be sampled because of logistic considerations. Sampling at numerous sites occurs over a 1- or 2-day period, commonly in remote regions. Because of the short holding time for bacteria (6 hours for fecal coliform, 24 hours for total coliform), we are unable to sample efficiently and regularly collect bacteria samples and comply with the required holding times.

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

7. Chain-of-Custody Procedures

Sample containers will be labeled with the site name and well or spring 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.

8. Quality Assurance/Quality Control Procedures

A. 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 are filtered on site. Sample collection equipment such as bailers and buckets will be 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.

B. Equipment Calibration

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

C. 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 Nonpoint 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. Spring samples will be collected as close to the spring resurgence as possible. If inhospitable terrain prohibits spring access, a decontaminated Teflon bucket attached to a new polypropylene rope may be lowered to the spring to collect the sample. Samples for pesticide analysis will be collected using a stainless steel bucket.

Duplicates and Blanks

Duplicate samples will be collected for at least 10 percent of all samples in order to check reproducibility and provide QA/QC control. At least one duplicate sample will be submitted with each batch of samples, regardless of the number of samples in the batch. Blanks of deionized water will be submitted at least once per quarter. Blanks will be collected, filtered, and preserved in the same manner as a sample. According to Division of Environmental Services accepted procedures, duplicate analyses will be accepted if they are within 20 percent relative standard deviation. If unacceptable results are found, samples will be reanalyzed and field records will be examined to determine the cause.

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.

9. References Cited

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.

Quinlan, J.F., ed., 1987, Qualitative water-tracing with dyes in karst terrains—Practical karst hydrogeology, with emphasis on groundwater monitoring: National Water Well Association, 26 p.

CHAIN OF CUSTODY RECORD
NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET
DIVISION OF WATER - GROUNDWATER BRANCH - NPS BMU 3 Expanded Sampling Project

Site Identification	**Collection Date/Time**	**Field Measurements**
Location:	Date: _____	Temp: _____ °C
County:		pH: _____
AKGWA #:	Time: _____	Cond: _____ µmhos

Sampler ID: _____

Division for Environmental Services Samples

Analysis Requested	**Container Size, Type**	**Preservation Method**	**Parameters**	**Analysis Requested**	**Container Size, Type**	**Preservation Method**	**Parameters**
	1000 ml Plastic	Cool to 4ºC	**Bulk Parameters IC Scan** (includes Chloride, Fluoride, Nitrate-N, Nitrite-N, Sulfate, Ortho-P) (Method 300.1; holding time 48 hrs) **Alkalinity, Conductivity, pH, TSS, TDS** (Methodds: 310.1, 120.1, 150.1, 160.2, 160.1, respectively)		1000 ml Rigid Plastic	Filtered HNO_3 Cool to 4ºC	**Dissolved Metals by ICP** plus Arsenic, Lead, Mercury, Selenium (Method 200.7)
	1000 ml Plastic	H_2SO_4 Cool to 4ºC	**NH_3/TKN/TOC/Total P** (Methods: 350.1, 351.1, 415.1, 365.4, respectively; holding time 28 days)		1000 ml Rigid Plastic	HNO_3 Cool to 4ºC	**Total Metals by ICP** plus Arsenic, Lead, Mercury, Selenium (Method 200.7)
	3 - 4 ml VOA vial and field blank	HCl	**VOC's (report MTBE)** (Method 8260; holding time 14 days)		1000 ml Glass	Cool to 4ºC	**N/P Pesticides** (Method 507; holding time 7 days)
	1000 ml Glass	Cool to 4ºC	**Herbicides** (Method 515.1; holding time 7 days)		1000 ml Glass	Cool to 4ºC	**Pesticides/PCBs** (Method 508; holding time 7 days)

Signatures:

Relinquished by: _____ Date: _____ Time: _____

Received by: _____

Relinquished by: _____ Date: _____ Time: _____

Received by: _____

Sample #: _____ Report #: _____

(revised 4/18/2000 per Lee Ruggles's e-mail)