

# **Regional Groundwater Quality in Watersheds of the Upper Cumberland, Lower Cumberland, and Lower Tennessee Rivers, and the Jackson Purchase Region (Kentucky Basin Management Unit 3)**

**R. Stephen Fisher<sup>1</sup>  
Bart Davidson<sup>1</sup>  
Peter T. Goodman<sup>2</sup>**

## **Abstract**

The Kentucky Geological Survey and the Kentucky Division of Water are evaluating groundwater quality throughout the commonwealth to determine regional conditions, assess impacts of nonpoint-source contaminants, provide a baseline for tracking changes, and provide essential information for environmental-protection and resource-management decisions. This report summarizes expanded groundwater monitoring activities and groundwater quality in watersheds of the Upper Cumberland River, Lower Cumberland River, Tennessee River, and the Jackson Purchase Region (Kentucky Basin Management Unit 3).

Thirty wells and springs were sampled seasonally between the summer of 2000 and the spring of 2001, and analyzed at the Kentucky Division of Environmental Services Laboratory. Analytical results for selected water properties, major and minor inorganic ions, metals, nutrients, pesticides, and volatile organic chemicals were combined with data retrieved from the Kentucky Groundwater Data Repository. The repository is maintained by the Kentucky Geological Survey and contains reports received from the Division of Water's Ambient Groundwater Monitoring Program as well as results of investigations by the U.S. Geological Survey, U.S. Environmental Protection Agency, U.S. Department of Energy, Kentucky Geological Survey, Kentucky Division of Pesticide Regulation, and other agencies. Statistics such as the number of measurements reported, the number of sites sampled, quartile values (maximum, third quartile, median, first quartile, and minimum), and the number of sites at which water-quality standards were exceeded summarize the data, and probability plots illustrate the data distribution. Maps show well and spring locations and sites where water-quality standards were met or exceeded. Box-and-whisker diagrams compare values between physiographic regions, major watersheds, wells and springs, and total versus dissolved metals. Plots of analyte concentrations versus well depth compare groundwater quality in shallow, intermediate, and deep groundwater flow systems.

Table A-1 summarizes the findings. General water properties (pH, total dissolved solids, total suspended solids, electrical conductance, and hardness), inorganic anions (chloride, sulfate, and fluoride), and metals (arsenic, barium, mercury, iron, and manganese) are primarily controlled by bedrock lithology. Some exceptionally high values of con-

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<sup>1</sup>Kentucky Geological Survey

<sup>2</sup>Kentucky Division of Water

ductance, hardness, chloride, and sulfate may be affected by oil and gas production, and some exceptionally low pH values may indicate the input of acid mine drainage. Nutrient concentrations (ammonia, nitrate, nitrite, orthophosphate, and total phosphorus) show a strong potential contribution from agricultural and waste-disposal practices. Synthetic organic chemicals such as pesticides (2,4-D, alachlor, atrazine, cyanazine, metolachlor, and simazine) and volatile organic compounds (benzene, ethylbenzene, toluene, xylene, and MTBE<sup>1</sup>) do not occur naturally in groundwater. Detection of these man-made chemicals in groundwater must be attributed to contamination. These synthetic chemicals are detected more commonly in springs and shallow wells than in deeper wells, indicating that the shallow groundwater system is particularly vulnerable to nonpoint-source contamination.

**Table A1.** Summary of nonpoint-source effects on groundwater quality in Kentucky Basin Management Unit 3.

|                                   | Parameter              | No Clear Evidence for Nonpoint-Source Impact on Groundwater Quality | Some Evidence for Nonpoint-Source Impact on Groundwater Quality | Clear Evidence for Nonpoint-Source Impact on Groundwater Quality |
|-----------------------------------|------------------------|---|---|--|
| <b>Water Properties</b>           | Conductance            |   | X   |  |
|                                   | Hardness               |   | X   |  |
|                                   | pH                     |   | X   |  |
|                                   | Total dissolved solids | X   |   |  |
|                                   | Total suspended solids | X   |   |  |
| <b>Inorganic Ions</b>             | Chloride               |   | X   |  |
|                                   | Sulfate                |   | X   |  |
|                                   | Fluoride               | X   |   |  |
| <b>Metals</b>                     | Arsenic                | X   |   |  |
|                                   | Barium                 | X   |   |  |
|                                   | Iron                   | X   |   |  |
|                                   | Manganese              | X   |   |  |
|                                   | Mercury                | X   |   |  |
| <b>Nutrients</b>                  | Ammonia-nitrogen       |   | X   |  |
|                                   | Nitrate-nitrogen       |   |   | X  |
|                                   | Nitrite-nitrogen       | X   |   |  |
|                                   | Orthophosphate         |   | X   |  |
|                                   | Total phosphorus       |   | X   |  |
| <b>Pesticides</b>                 | 2,4-D                  |   |   | X  |
|                                   | Alachlor               |   |   | X  |
|                                   | Atrazine               |   |   | X  |
|                                   | Cyanazine              |   |   | X  |
|                                   | Metolachlor            |   |   | X  |
|                                   | Simazine               |   |   | X  |
| <b>Volatile Organic Compounds</b> | Benzene                |   |   | X  |
|                                   | Ethylbenzene           |   |   | X  |
|                                   | Toluene                |   |   | X  |
|                                   | Xylenes                |   |   | X  |
|                                   | MTBE                   |   |   | X  |

<sup>1</sup> Methyl tertiary-butyl ether

# Introduction

## **Purpose**

Evaluating groundwater quality, its suitability for various uses, the sources of chemicals present, and the potential impacts of nonpoint-source contaminants is essential for making wise decisions concerning the use, management, and protection of this vital resource. Regional groundwater quality in Kentucky is being investigated through two related programs: the Kentucky Division of Water conducts and reports on statewide groundwater-quality monitoring, and the Kentucky Geological Survey, in cooperation with DOW, publishes summary reports of regional groundwater quality.

DOW operates an ambient groundwater monitoring program that collects and analyzes samples from approximately 120 wells and springs throughout the commonwealth quarterly each year. DOW also conducts expanded groundwater monitoring in which one of the five Basin Management Units established by the Division of Water Watershed Management Framework (Kentucky Division of Water, 1997) is selected each year for more intensive sample collection and analysis. Approximately 30 wells and springs in the selected BMU are sampled quarterly for four quarters. The resulting analytical data are added to the DOW groundwater-quality database and transferred to the Kentucky Groundwater Data Repository, maintained by KGS. The data repository was created in 1990 by the Kentucky General Assembly to archive groundwater data collected by State and Federal agencies, universities, and other researchers. It also contains analytical results from groundwater studies by the U.S. Geological Survey, U.S. Environmental Protection Agency, U.S. Department of Energy, University of Kentucky researchers, and others.

Until recently, there were no regional reports of groundwater quality that included nonpoint-source chemicals. DOW summarized water quality and nonpoint-source chemicals in wells and springs in the Salt and Licking River Basins (Webb and others, 2003), and KGS and DOW prepared a similar report on groundwater quality in basins of the Upper Cumberland, Lower Cumberland, Tennessee, Green, and Tradewater Rivers and watersheds of tributaries to the Ohio and Mississippi Rivers in the Jackson Purchase Region (Fisher and others, 2003).

The purpose of this report is to summarize the results of expanded groundwater monitoring in watersheds of the Upper Cumberland River, Lower Cumberland River, Tennessee River, and tributaries of the Mississippi River and Ohio River in the Jackson Purchase Region and evaluate groundwater quality using

the new data and all other analytical records stored in the Groundwater Data Repository.

## **Goals**

The goals of this report are to (1) compile reliable groundwater-quality analyses from available sources for wells and springs in BMU 3, (2) summarize groundwater properties and the concentrations of selected inorganic and organic constituents, (3) map sample locations and identify sites where concentrations exceed critical values, (4) interpret the sources of chemicals found in groundwater, (5) determine whether nonpoint-source chemicals have entered the groundwater system, and (6) interpret and distribute the findings.

The results of this evaluation (1) provide a basis for identifying anomalous concentrations of dissolved or suspended chemicals in groundwater, (2) identify areas where nonpoint-source chemicals have entered the groundwater system and where future nonpoint-source investigations and implementation of best management practices are needed, (3) provide information for watershed assessment reports, (4) provide groundwater-quality data to the Kentucky Division of Water Groundwater Protection programs, (5) assist the Division of Water Wellhead Protection program in setting priorities for protection areas and activities, including the development, implementation, and evaluation of best management practices, and (6) provide critical information for long-term protection and management of groundwater resources.

## **Background**

Evaluating groundwater quality is particularly important in Kentucky because its use is extensive and will continue to be so. The Division of Water estimates that approximately 1.3 million Kentuckians are served by public water systems that rely on groundwater, in whole or part, as their source. In addition, approximately 500,000 Kentuckians are estimated to rely on private supplies of groundwater, as wells or springs, for their primary source of drinking water. Groundwater will continue to be important to Kentuckians because economic and logistical factors make replacing groundwater with surface-water supplies expensive or impractical, particularly in rural areas. An estimated 250,000 Kentuckians will still depend on private, domestic water supplies in the year 2020 (Kentucky Geological Survey, 1999). Because it is so important, the quality of Kentucky's groundwater must be evaluated and protected in the interest of human health, ecosystem preservation, and the needs of a growing population and economy.

This study focuses on the quality of regional groundwater that is not known to be affected by point-

source contamination. Both natural processes and man-made constituents affect groundwater quality. The major natural processes that contribute cations, anions, metals, nutrients, and sediment to groundwater are (1) dissolution of atmospheric gases as rain falls through the atmosphere, (2) dissolution of soil particles and physical transport of chemicals and sediment as rainfall flows across the land surface, (3) dissolution of soil gases and reactions with minerals and organic material in the soil zone above the water table, and (4) reactions with gases, minerals, and organic material beneath the water table.

Groundwater quality is also affected by activities that contribute synthetic organic chemicals, such as pesticides, fertilizers, and volatile organic compounds, as well as cations, anions, metals, nutrients, and sediment, to the water system. Nearly all activities that threaten surface waters and ecosystems also endanger groundwater systems. Agriculture, confined animal feeding operations, forestry, mining, oil and gas production, waste disposal, and stormwater runoff can deliver pesticides, fertilizers, nutrients, metals, and hydrocarbons to groundwater.

### **Previous Investigations**

Few previously published reports evaluate the presence of nonpoint-source chemicals in groundwater in the project area. In the 1960's and early 1970's the U.S. Geological Survey published reconnaissance studies of the geology, groundwater supplies, and general groundwater quality in Kentucky. These reports include the Hydrologic Atlas series, each covering several counties (available at [www.uky.edu/KGS/water/library/USGSHA.html](http://www.uky.edu/KGS/water/library/USGSHA.html)), and more comprehensive reports for the Jackson Purchase Region (MacCary and Lambert, 1962; Davis and others, 1973), Eastern Kentucky Coal Field (Price and others, 1962), and the Mississippian Plateau Region, herein referred to as the Eastern and Western Pennyroyal Regions (Brown and Lambert, 1963). These reports considered only major and minor inorganic ions and nitrate; other nutrients, metals, and synthetic organic chemicals were not considered. Other studies took a similar approach to smaller areas: the Paducah area of the Jackson Purchase Region (Pree and others, 1957) and the Scottsville area of the Western Pennyroyal Region (Hopkins, 1963).

Sprinkle and others (1983) summarized general groundwater quality throughout Kentucky. The Kentucky Geological Survey (1999) summarized groundwater supply and general groundwater quality throughout the state (available at [kgsweb.uky.edu/download/wrs/GWTASK1.PDF](http://kgsweb.uky.edu/download/wrs/GWTASK1.PDF)). Carey and Stickney (2001, 2002a, b, 2004a-p, 2005a-p) summarized groundwater resources for the counties covered in this

report, using groundwater quality information from the Hydrologic Atlases and county-specific information compiled from many sources (available at [www.uky.edu/KGS/water/library/gwatlas](http://www.uky.edu/KGS/water/library/gwatlas)).

Carey and others (1993) surveyed selected groundwater-quality parameters, including nutrients and pesticides, in private groundwater supplies. In a much more detailed study, Currens (1999) reported on water quality, pesticides, and nutrients in a karst system in Logan County (Western Pennyroyal Region). Two other sources of largely uninterpreted analytical data contributed significantly to the database used here. Faust and others (1980) summarized the results of cooperative groundwater investigations involving the KGS and other State, Federal, and local agencies. The National Uranium Resource Evaluation program was a second source of analyses of groundwater, surface water, and stream sediments (Smith, 2001). Digital records from both of these reports are stored in the Kentucky Groundwater Data Repository and were used in this report. None of these reports specifically addressed regional groundwater quality or the presence of nonpoint-source chemicals such as nutrients, pesticides, or other synthetic organic compounds on groundwater quality.

### **Project Area**

The Kentucky Division of Water has grouped Kentucky's major river basins into five Basin Management Units (Fig. 1). The project area includes watersheds of the Upper Cumberland River, Lower Cumberland River, Tennessee River, tributaries to the Mississippi River in the Jackson Purchase Region; and tributaries of the Ohio River adjacent to these major watersheds in southwestern and western Kentucky (BMU 3). Five of Kentucky's eight physiographic regions are included in the project area, each distinguished by unique bedrock geology, topography, and soil types (McDowell, 1986; Newell, 1986). This physiographic framework is critical to understanding groundwater quality because it largely controls the natural occurrence of major and minor inorganic solutes and metals in groundwater. It also strongly influences land use, urban and commercial development, and the potential presence of nonpoint-source contaminants.

The project area includes the mountainous terrain of the Eastern Kentucky Coal Field, a very small section of the Knobs Region, the karst landscape of the Eastern and Western Pennyroyal Regions, and the largely agricultural Jackson Purchase Region (Fig. 1). Deeply incised sandstone, shale, and coal layers that are essentially horizontal throughout most of the area, but are nearly vertical along the Pine Mountain Overthrust Fault in southeastern Kentucky, characterize the

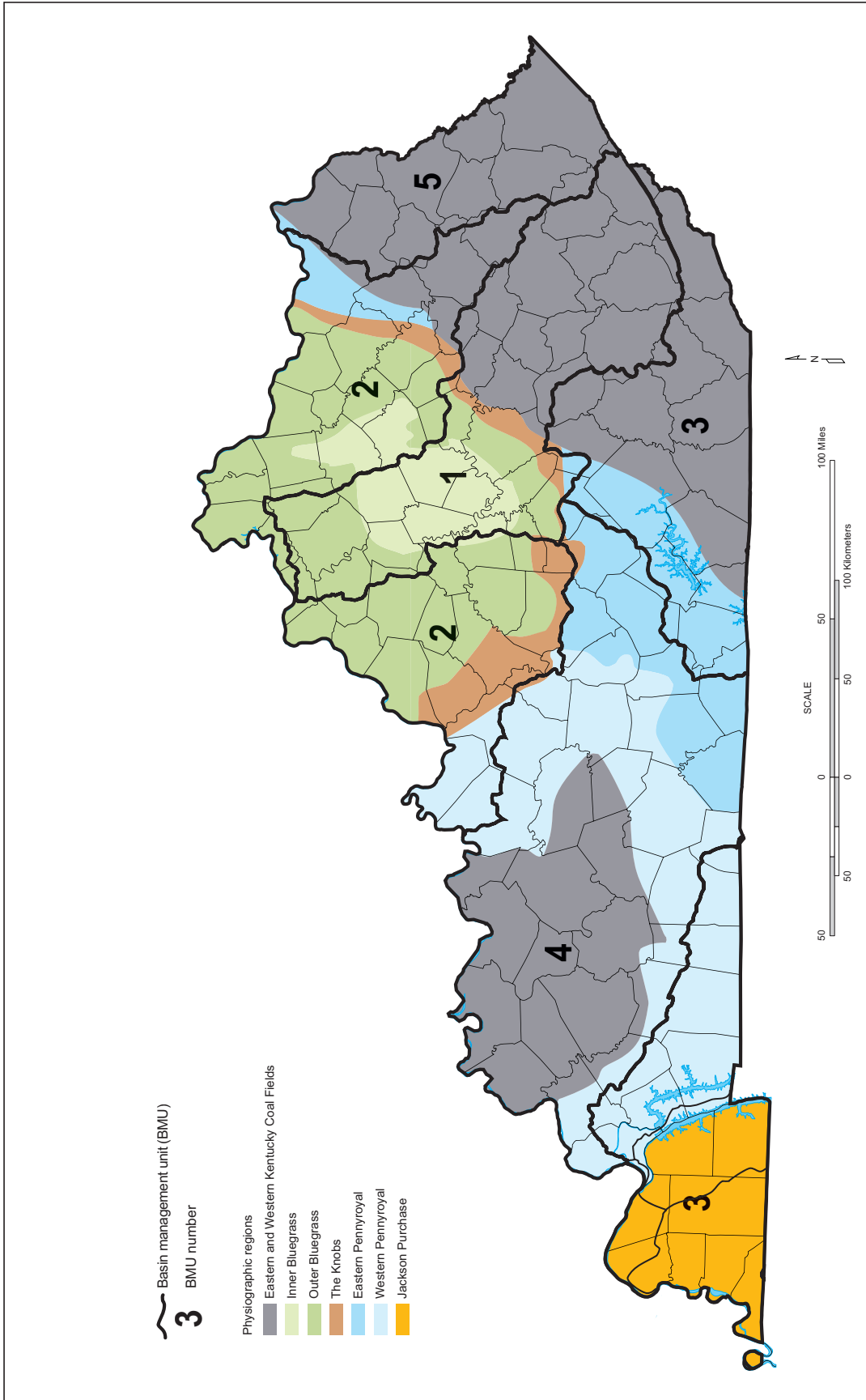


Figure 1. Physiographic regions, Basin Management Units, and major river watersheds in BMU 3.

Eastern Kentucky Coal Field. Steep hillsides separate narrow, flat river valleys from sharp, sinuous mountain crests (Newell, 1986). The Eastern Pennyroyal and Western Pennyroyal Regions consist mainly of thick, horizontally bedded limestone with minor, thin shales. The topography is flat to gently rolling with well-developed karst features such as sinkholes, springs, and caverns (Newell, 1986). The Jackson Purchase is underlain by unconsolidated to poorly consolidated gravel, sand, silt, and clayey sediments (Newell, 1986).

Land uses and nonpoint-source-pollution threats to groundwater quality in BMU 3 include oil and gas production; abandoned or improperly plugged oil and gas wells; active and abandoned coal mines; unplugged coal coreholes; leaking sewage disposal systems; deforested areas in the Eastern Kentucky Coal Field; and farm land, urban centers, and confined animal feeding operations in the Eastern and Western Pennyroyal and Jackson Purchase Regions (Kentucky Division of Water, 2000). Groundwater is particularly vulnerable to nonpoint-source contamination in the karst regions of the Pennyroyal because of the well-developed network of sinkholes, caverns, and springs. Groundwater is

also vulnerable where sand and gravel outcrops allow rapid recharge to aquifers in the Jackson Purchase.

BMU 3 includes Adair, Ballard, Bell, Caldwell, Calloway, Carlisle, Casey, Christian, Clinton, Crittenden, Cumberland, Fulton, Graves, Harlan, Hickman, Jackson, Knox, Laurel, Letcher, Lincoln, Livingston, Logan, Lyon, Marshall, McCracken, McCreary, Metcalfe, Monroe, Pulaski, Rockcastle, Russell, Simpson, Todd, Trigg, Wayne, and Whitley Counties.

### **Hydrogeologic Unit Codes**

The U.S. Geological Survey has assigned Hydrogeologic Unit Codes to watersheds to identify regions, subregions, accounting units, and cataloging units (USGS, 1976). The HUC designations of watersheds in BMU 3 are listed in Table 1.

### **Groundwater Sensitivity Regions**

The potential for groundwater contamination is not uniform throughout the study area. The vulnerability of groundwater to nonpoint-source contamination varies geographically across Kentucky, and verti-

**Table 1.** Watershed names, HUC numbers, and physiographic regions.

| HUC           | Watershed Name and Physiographic Region  |
|---------------|--|
| <b>051301</b> | <b>Upper Cumberland River<br/>(Eastern Kentucky Coal Field, Knobs, Eastern Pennyroyal)</b>   |
| 05130101      | Upper Cumberland River   |
| 05130102      | Rockcastle River   |
| 05130103      | Cumberland River   |
| 05130104      | South Fork Cumberland River  |
| 05130105      | Dale Hollow Lake   |
| <b>051302</b> | <b>Lower Cumberland River (Western Pennyroyal)</b>   |
| 05130205      | Barkley Lake, Cumberland River   |
| 05130206      | Lower Cumberland River, Red River  |
| <b>051402</b> | <b>Ohio River Tributaries (Jackson Purchase)</b>   |
| 05140206      | Ohio River, Massac Creek   |
| <b>060400</b> | <b>Lower Tennessee River (Western Pennyroyal, Jackson Purchase)</b>                          |
| 06040005      | Tennessee River, Kentucky Lake   |
| 06040006      | Tennessee River, Clarks River  |
| <b>080101</b> | <b>Mississippi River Tributaries (Jackson Purchase)</b>                                      |
| 08010100      | Mississippi River  |
| <b>080102</b> | <b>Mayfield Creek, Obion Creek, Bayou de Chien, Mississippi River<br/>(Jackson Purchase)</b> |
| 08010201      | Mayfield Creek, Obion Creek, Bayou de Chien  |
| 08010202      | Mississippi River, Reelfoot Lake   |

cally at any given location, in response to both natural and man-made factors.

Among the most important natural controls on the transport of pollutants to the groundwater system are physiography (principally the topography, relief, land slope, and presence or absence of sinkholes or caves), soil type and thickness, bedrock type, bedrock structure (principally the bedrock porosity and permeability and the presence or absence of faults, fractures, or solution conduits), and depth to groundwater. Overprinted on the natural environment are man-made factors such as the type of land use, nature and amount of chemicals applied to agricultural and urban landscapes, wastewater and sewage-disposal practices, and the effects of resource extraction (principally oil and gas production and coal mining).

Recognizing the need to develop a flexible program for groundwater protection, the Kentucky Division of Water developed a method for rating and delineating regions of different groundwater sensitivity (Ray and O'dell, 1993) and published a map showing the various groundwater sensitivity regions throughout the commonwealth (Ray and others, 1994). Ray and O'dell (1993) found that the natural factors controlling the potential for contamination of the uppermost (nearest to land surface) aquifer can be assessed from three factors: (1) the potential ease and speed of vertical infiltration, (2) the maximum potential flow velocity, and (3) the potential for dilution by dispersion after a chemical enters the aquifer.

Groundwater sensitivity to nonpoint-source contamination generally decreases with depth as a result of the same factors: (1) infiltration is slower and more tortuous, allowing for degradation and dilution of the chemicals, (2) flow velocities in deep groundwater systems are slower, allowing for additional degradation and dilution of nonpoint-source chemicals, and (3) dispersion and dilution are greater because deep groundwater systems contain water from large recharge areas.

Within the study area, the sensitivity of shallow groundwater to nonpoint-source contamination can best be summarized by physiographic region (Ray and others, 1994). The uppermost groundwater system is rated as moderately sensitive in the Eastern Kentucky Coal Field, extremely sensitive in the Eastern and Western Pennyroyal Regions, and slightly to moderately sensitive in the Jackson Purchase Region (Ray and others, 1994).

Local groundwater sensitivity may be very different from these regional assessments; however, local conditions cannot be assessed in this regional summary of groundwater quality. Well depth is an approximate indicator of whether a shallow, intermediate,

or deep groundwater system is being sampled. Two factors limit the usefulness of well depth as an indicator of groundwater system, however. First, many wells have no depth recorded, are uncased throughout much of their length and thus collect water from various depths, or are drilled deeper than needed to serve as a water-storage system. Second, a shallow well may actually intercept a deep groundwater flow system if the well is located near the discharge region of the groundwater flow system.

## Methods

### *Site Selection for Expanded Monitoring*

The groundwater sampling program is intended to represent the various physiographic, geologic, land-use, and demographic settings in the river basins. Resource limitations preclude drilling new wells; therefore, candidate sites were selected from existing wells and springs. The site selection process followed three steps.

1. Thirty 7.5-minute quadrangles were selected at random in BMU 3. To avoid selection bias, each quadrangle in BMU 3 was assigned a number, and 30 numbers were drawn at random. To be eligible for selection, the center of each quadrangle had to fall within BMU 3; quadrangles in which groundwater monitoring was currently being performed were not considered. If there were no suitable wells or springs in the selected quadrangle, an adjacent quadrangle was selected.
2. Within each selected quadrangle, potential groundwater sample sites were ranked according to type, use, condition, and accessibility. Large springs were preferred over wells because such springs collect water from large basin areas and are more sensitive to nonpoint-source pollution impacts to groundwater. Public wells or nonregulated public springs used for domestic purposes were chosen over private wells or wells used for livestock or irrigation. Springs protected from surface runoff and properly constructed wells were preferred to avoid sample contamination. Readily accessible springs and wells were selected over sites in remote locations or sites with limited access.
3. Final site selections were made only after field inspection to ensure that seasonal monitoring was feasible and after obtaining permission from owners. Sample sites are listed in Table 2.

**Table 2.** Sample sites for expanded monitoring in Basin Management Unit 3.

| Site Name                       | AKGWA No. | County     | Latitude  | Longitude |
|---------------------------------|-----------|------------|-----------|-----------|
| Alvin Feltner well              | 00005772  | Laurel     | 37.217222 | 83.958333 |
| Barnett Spring                  | 90002556  | Lyon       | 36.975917 | 87.984083 |
| Bee Rock CG Spring              | 90002544  | Laurel     | 37.021833 | 84.328472 |
| Berberich Spring                | 90002551  | Adair      | 36.983889 | 85.210000 |
| Cartwright Spring               | 90002552  | Clinton    | 36.756111 | 85.086139 |
| Cash Spring                     | 90002554  | Lyon       | 37.119528 | 88.059972 |
| Clover Lick Spring              | 90002547  | Harlan     | 36.948583 | 82.997528 |
| Cold Spring                     | 90002553  | Whitley    | 36.839444 | 84.281889 |
| Flat Spring                     | 90002560  | Wayne      | 36.799361 | 84.889000 |
| Fletcher Cave                   | 90002548  | Pulaski    | 37.187583 | 84.548222 |
| Happy Hollow Spring             | 90001832  | Clinton    | 36.689167 | 85.140278 |
| Henry Armstrong well            | 00011386  | Calloway   | 36.567500 | 88.461361 |
| Howard Spring                   | 90002566  | McCreary   | 36.854583 | 84.490361 |
| Jenson Spring on Straight Creek | 90002545  | Bell       | 36.776389 | 83.618861 |
| Jones Ridge Road Spring         | 90002549  | Cumberland | 36.877639 | 85.383333 |
| Lakeway Shores well             | 00014657  | Calloway   | 36.589167 | 88.137222 |
| Lower Skegg Creek Spring        | 90002546  | Rockcastle | 37.235000 | 84.275000 |
| Loyd Dick Spring                | 90002561  | Pulaski    | 37.163472 | 84.706472 |
| Marrowbone Spring               | 90002563  | Metcalfe   | 36.846028 | 85.632417 |
| Mason/Pembroke Spring           | 90001150  | Christian  | 36.763167 | 87.356250 |
| Max Wilson well                 | 00000657  | Fulton     | 36.526944 | 89.073056 |
| Mill Springs                    | 90001822  | Wayne      | 36.934389 | 84.778528 |
| Mount Vernon Spring             | 90002550  | Hickman    | 36.631278 | 88.967778 |
| Mullins Station Spring          | 90002557  | Rockcastle | 37.344722 | 84.228611 |
| Nichols Spring                  | 90002562  | Pulaski    | 37.179167 | 84.458639 |
| Peeled Dogwood Spring           | 90002565  | McCreary   | 36.747778 | 84.394250 |
| Russell Chapel Spring           | 90002555  | Calloway   | 36.660750 | 88.136167 |
| Shields/Benito Spring           | 90002559  | Harlan     | 36.902083 | 83.128972 |
| Sinking Creek Spring            | 90002558  | Laurel     | 37.096472 | 84.178750 |
| Terry Fork Spring               | 90002564  | Harlan     | 36.824583 | 83.404917 |
| Whitley County/Rockholds well   | 00027904  | Whitley    | 36.828333 | 84.110833 |

## Sample Collection for Expanded Monitoring

Samples were collected seasonally from July 2000 through May 2001. Conductivity, temperature, and pH were measured at each site and recorded in a field log book. Meters and electrodes were calibrated using standard buffer solutions and cleaned after each use according to manufacturers' specifications.

Samples for measurement of chemical constituents were collected and preserved as necessary for laboratory analysis. All materials that contacted the sample were either new, disposable, or were decontaminated prior to and after each use. Sample containers were labeled with the site name and well or spring identification number, collection date and time, analysis requested, preservation method, and collector's initials.

Bacteria were not sampled for logistical reasons. Sample collection trips visited six to 12 sites over a 1- to 2-day period, commonly in remote regions. The short holding time for bacteria (6 hours for fecal coliform, 24 hours for total coliform) prohibited collecting

aliquots for bacterial analysis while maintaining sampling efficiently for all other parameters.

Duplicate samples were collected for at least 10 percent of all samples in order to check reproducibility and provide quality assurance/quality control. One duplicate sample was submitted with each batch of samples. Field blanks of deionized water were collected, filtered, and preserved in the same manner as a sample and submitted once per quarter.

Sample container, preservation, and holding time requirements are outlined in the Kentucky Division of Water's "Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects," prepared by the Water Quality Branch. Sampling personnel completed a chain-of-custody record developed in conjunction with the Division of Environmental Services Laboratory for each sample. Specific sample collection methods are documented in the project QC/QC plan, which was approved by the Division of Water before sampling began. The approved QA/QC plan is attached as Appendix A.



## Sample Analysis for Expanded Monitoring

All samples except those collected in the fall of 2000 were delivered to the Kentucky Division of Environmental Services Laboratory for analysis. Groundwater collected in November and December of 2000 was analyzed at the Kentucky Geological Survey because the DES Laboratory was required to dedicate all resources to evaluating the effects of a spill at a coal-slurry pond. At both laboratories, major and minor inorganic ions, nutrients, total organic carbon, pesticides, herbicides, insecticides, fungicides, and dissolved and total metals were determined according to EPA-approved laboratory procedures. The analytical results were entered into the Kentucky Department of Environmental Protection Consolidated Groundwater Database and copied to the Kentucky Groundwater Data Repository.

## Data Analysis and Summary

Analytical results from the expanded groundwater monitoring programs were combined with records of groundwater analyses from wells and springs in BMU 3 extracted from the Kentucky Groundwater Data Repository. The intent was to extract and summarize analyses that would characterize regional groundwater quality. Some of the anomalous values that were included in the resulting data sets may represent local or point-source contamination; however, there was no basis in the data reports for excluding those results. Determining whether these results were naturally occurring extreme values, inaccurate data entries, or are the result of pollutants would require reviewing the original sample collection reports or visiting the site. Such activities were beyond the scope of this project.

The following steps were taken to summarize and evaluate the analytical data.

- 1. Query the repository database for reports of analyses.** Analytical reports were selected for groundwater-quality constituents that either determine the suitability of the water for various uses, provide geochemical signatures that characterize the regional groundwater flow system, have recognized or suspected impacts on human health, or record the impacts of nonpoint-source contaminants on groundwater. The parameters selected were:

**General properties:** pH, total dissolved solids, conductance, hardness, and total suspended solids

**Inorganic anions:** chloride, fluoride, sulfate

**Metals:** arsenic, barium, iron, manganese, mercury

**Nutrients:** ammonia, nitrate, nitrite, orthophosphate, total phosphorus

**Pesticides:** alachlor, atrazine, cyanazine, metolachlor, simazine

**Volatile organic compounds:** benzene, ethylbenzene, toluene, xylenes, MTBE

Summaries and discussions of results are based on analytical records in the Kentucky Groundwater Data Repository as of June 2002.

Both dissolved concentrations (measured from a sample that had been filtered to remove suspended particulate material) and total concentrations (measured from an unfiltered sample) were retrieved from the database for metals.

Many of the analytes of interest have been reported under a variety of names, and not all analytical results are identified by unique CAS numbers (Chemical Abstract Service registry numbers), so queries were written to return all variations of the analyte name. For example, phosphorus measurements are reported as "orthophosphate," "orthophosphate-P ( $\text{PO}_4\text{-P}$ )," "phosphate," "phosphate-total," "phosphate-ortho," "phosphorus," "phosphorus-ortho," "phosphorus-total," "phosphorus-total by ICP," and "phosphorus-total dissolved." The results were then inspected to ensure that each resulting data set contained the appropriate chemical species. All reported analytical units were converted to milligrams per liter.

Samples collected for the Resource Conservation and Recovery Act or solid waste regulatory programs were excluded because these are sites of known or suspected point-source contamination. Analyses of volatile organic compounds from monitoring wells at underground storage tank sites were excluded for the same reason.

Each sample site was assigned a six-digit HUC number, major watershed name, and physiographic region designation so that the data could be grouped into these categories. GIS coverages of six-digit HUC's and physiographic regions were obtained from the Kentucky Geological Survey Web site ([www.uky.edu/KGS/gis/intro.html](http://www.uky.edu/KGS/gis/intro.html)).

- 2. Delete records that do not provide useful information.** The U.S. Environmental Protection Agency has established maximum contaminant levels for chemicals that present health risks. Some analytical results in the ground-

water data repository were reported only as "less than" a detection limit, where the detection limit was greater than the MCL or other threshold value. These records do not provide useful analytical data for this report and so were eliminated from the data sets.

3. **Count the number of analytical results and the number of sites sampled for each constituent.** Many wells and springs were sampled more than once, so there may be more than one reported concentration for any given analyte at a particular site. The number of individual sites was determined by counting unique location identification numbers associated with the analytical records.
4. **Determine minimum, first quartile, median, third quartile, and maximum concentrations.** Water-quality data are generally not normally distributed and may contain anomalously low minimum values and anomalously high maximum values. The combined effect of a non-normal distribution and extreme outlier values is that parametric statistical measures such as mean and standard deviation do not efficiently describe the data. Nonparametric statistical measures such as quartile values and interquartile range provide a better description of the data population (see Helsel and Hirsch, 1992, for example).

The quartile values are:

- zero quartile value:** the minimum value; all other values are greater
- first quartile value:** the value that is greater than 25 percent of all values
- second quartile value:** the median value; greater than 50 percent of all values
- third quartile value:** the value that is greater than 75 percent of all values
- fourth quartile value:** the maximum value

Maximum and minimum concentrations may be anomalous, but the median value and the interquartile range (range of values between the first and third quartile values, also equal to the central 50 percent of the data) provide an efficient summary of the data. Many analytical results are censored data; that is, they are reported as less than a detection limit rather than as an accurately measured concentration. The preferred treatment of censored data depends on the purpose of the analysis. For example, the EPA has established guidelines for treating censored data in Resource Conservation and Recovery Act investigations

(U.S. EPA, 1992). The goals of this report are to summarize ambient groundwater quality and to locate regions affected or threatened by nonpoint-source contamination. Therefore, censored data were treated as if the analyte concentration was equal to the detection limit, but the censored data were ranked below actual measurements at that value when quartile values were determined. For example, a value reported as less than a detection limit of 0.0004 mg/L was ranked below a measured value of 0.0004 mg/L and above a measured value of 0.0003 mg/L for the quartile determinations.

5. **Determine the number of sites at which measurements exceeded water-quality standards.** Water-quality standards were provided by the Kentucky Division of Water (Table 3). Because many samples may have been analyzed from a particular well or spring over time, the number of sites at which parameters exceed critical values is a better indicator of regional groundwater quality than the number of measurements that exceed those values.
6. **Map sample sites and use various symbols to represent concentration ranges and to show where MCL or other critical values were exceeded.** Maps show sample site locations, site distributions, concentration ranges, and areas where concentrations exceed MCL's or other critical values. Maps also reveal whether analyte values are randomly distributed or are related to watersheds, physiography, or land use.

Maps were generated using ArcView GIS 3.1. At the scale used in this report and depending on symbol size and shape, sites within a few thousand feet of each other may not be resolved as separate locations. Therefore, the maps are useful for illustrating the general location of sites where various criteria are met or exceeded, but they may not provide an accurate count of those sites.

7. **Use summary tables, cumulative probability plots, and box-and-whisker diagrams to summarize and illustrate the data and to compare analytical results between watersheds, physiographic regions, or other groupings.** Summary tables list the number of measurements and sites, quartile values, and the number of sites where concentrations exceed MCL's or other standard values for each BMU.

Probability plots (cumulative data plots) show the distribution of values as a percentage of the total number of analytical results. They

**Table 3.** Parameters and water-quality standards used for data summaries.

|                                   | <b>Parameter</b>                 | <b>Standard<br/>(mg/L unless otherwise noted)</b>  | <b>Source</b>                               |
|-----------------------------------|----------------------------------|--|---|
| <b>Water Properties</b>           | Conductance                      | 10,000 $\mu$ S   | Approximately corresponds to brackish water |
|                                   | Hardness (calcium and magnesium) | Soft: 0–17<br>Slightly hard: 18–60<br>Moderately hard: 61–120<br>Hard: 121–180<br>Very hard: > 180 | U.S. Geological Survey                      |
|                                   | pH                               | 6.5–8.5 pH units   | SMCL  |
|                                   | Total dissolved solids           | 500  | SMCL  |
|                                   | Total suspended solids           | 35   | KPDES                                       |
|                                   | Chloride                         | 250  | SMCL  |
| <b>Inorganic Ions</b>             | Sulfate                          | 250  | SMCL  |
|                                   | Fluoride                         | 4.0  | MCL   |
|                                   | Arsenic                          | 0.010  | MCL   |
|                                   | Barium                           | 2.0  | MCL   |
| <b>Metals</b>                     | Iron                             | 0.3  | SMCL  |
|                                   | Manganese                        | 0.05   | SMCL  |
|                                   | Mercury                          | 0.002  | MCL   |
| <b>Nutrients</b>                  | Ammonia-nitrogen                 | 0.110  | DEP   |
|                                   | Nitrate-nitrogen                 | 10.0   | MCL   |
|                                   | Nitrite-nitrogen                 | 1.0  | MCL   |
|                                   | Orthophosphate-phosphorus        | 0.04   | Texas surface-water standard                |
|                                   | Total phosphorus                 | 0.1  | NAWQA                                       |
| <b>Pesticides</b>                 | 2,4-D                            | 0.007  | MCL   |
|                                   | Alachlor                         | 0.002  | MCL   |
|                                   | Atrazine                         | 0.003  | MCL   |
|                                   | Cyanazine                        | 0.001  | HAL   |
|                                   | Metolachlor                      | 0.1  | HAL   |
|                                   | Simazine                         | 0.004  | MCL   |
| <b>Volatile Organic Compounds</b> | Benzene                          | 0.005  | MCL   |
|                                   | Ethylbenzene                     | 0.7  | MCL   |
|                                   | Toluene                          | 1.0  | MCL   |
|                                   | Xylenes                          | 10   | MCL   |
|                                   | MTBE                             | 0.050  | DEP   |

MCL: Maximum contaminant level allowed by EPA in drinking water. Higher concentrations may present health risks.  
SMCL: Secondary maximum contaminant level (EPA). Higher concentrations may degrade the sight, smell, or taste of the water.  
NAWQA: National Water-Quality Assessment Program, U.S. Geological Survey. Higher concentrations may promote eutrophication.  
HAL: Health advisory level. Higher concentrations may present concerns for human health.  
KPDES: Kentucky Pollution Discharge Elimination System. Standard set for water-treatment facilities.  
DEP: Kentucky Department for Environmental Protection risk-based concentration. Higher concentrations may present health risks.

the total number of analytical results. They provide an easy way to identify outlier values. The cumulative data plots in this report exclude the highest and lowest 0.1 percent of the values so that extremely high or low values do not compress the display of the majority of the data. Therefore, probability plots of data sets that contain more than 1,000 measurements do not show the absolute maximum and minimum values. Each plot also includes a straight line that shows the locus of points along which the data would fall if the measurements were normally distributed.

Box-and-whisker diagrams show the median value and the interquartile range, and illustrate how clustered or scattered analytical results are. The box extends from the first quartile value to the third quartile value, including the central 50 percent of the data. A center line within the box shows the median value, and a plus sign marks the sample mean. Whiskers extend from each edge of the box to minimum and maximum values, unless there are outside or far outside points, which are plotted separately. Outside points are values that are more than 1.5 times the interquartile range above the third quartile value or below the first quartile value; they are shown as squares. Far outside points are values that lie more than 3.0 times the interquartile range above the third quartile value or below the first quartile value; they are shown as squares with plus signs through them. The presence of far outside points indicates suspect values or a highly skewed distribution. Because most water-quality data are positively skewed, the plots compress the low range of data and emphasize the higher values. With the exception of iron and manganese, all analytes summarized in this report have median and third quartile (75th percentile) values that are less than the standards listed in Table 3. Therefore, the summary plots and graphs shown in this report focus attention on the higher concentrations that may exceed water-quality standards. Probability plots and

box-and-whisker plots were generated using Statgraphics Plus for Windows 4.1.

The approach for each analyte is:

1. Define the analyte, summarize common natural and nonpoint sources, list relevant water-quality criteria, and describe how excessive amounts affect water use and human health.
2. Summarize analytical reports by constructing summary data tables and cumulative data plots.
3. Show sample-site distribution and sites where water-quality standards are met or exceeded by mapping sample sites and concentration ranges.
4. Summarize data for each physiographic region by constructing box-and-whisker plots.
5. Summarize data for the Upper Cumberland, Lower Cumberland, Tennessee, Ohio, and Mississippi River watersheds by constructing box-and-whisker plots.
6. Evaluate the impact on shallow (less than 200 ft), intermediate (200 to 500 ft), and deep (greater than 500 ft) groundwater flow systems by using box-and-whisker plots to compare values from wells and springs, and by plotting concentrations versus well depth. Note that well depths may be misleading for two reasons. First, depth is not recorded for many wells; therefore, analyte concentrations from these sites cannot be evaluated with respect to depth. Second, the well depths that are recorded are total depths, not cased intervals or the depth of the water-producing strata.
7. Compare dissolved versus total concentrations if both measurements have been reported. If total concentrations are systematically greater than dissolved concentrations, the analyte is probably both truly dissolved in groundwater (represented by the dissolved concentration) and also associated with suspended particulate material (represented by the total concentration).
8. Summarize potential causes of observed concentrations and distribution of values, and evaluate potential nonpoint-source contributions to groundwater concentrations.