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# 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)

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## 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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[1] Kentucky Geological Survey
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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[1]) 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** |
|---|---|---|---|---|
| **Water Properties** | Conductance | | X | |
| | Hardness | | X | |
| | pH | | X | |
| | Total dissolved solids | X | | |
| | Total suspended solids | X | | |
| **Inorganic Ions** | Chloride | | X | |
| | Sulfate | | X | |
| | Fluoride | X | | |
| **Metals** | Arsenic | X | | |
| | Barium | X | | |
| | Iron | X | | |
| | Manganese | X | | |
| | Mercury | X | | |
| **Nutrients** | Ammonia-nitrogen | | X | |
| | Nitrate-nitrogen | | | X |
| | Nitrite-nitrogen | X | | |
| | Orthophosphate | | X | |
| | Total phosphorus | | X | |
| **Pesticides** | 2,4-D | | | X |
| | Alachlor | | | X |
| | Atrazine | | | X |
| | Cyanazine | | | X |
| | Metolachlor | | | X |
| | Simazine | | | X |
| **Volatile Organic Compounds** | Benzene | | | X |
| | Ethylbenzene | | | X |
| | Toluene | | | X |
| | Xylenes | | | X |
| | MTBE | | | X |

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[1] 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), 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). 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).

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

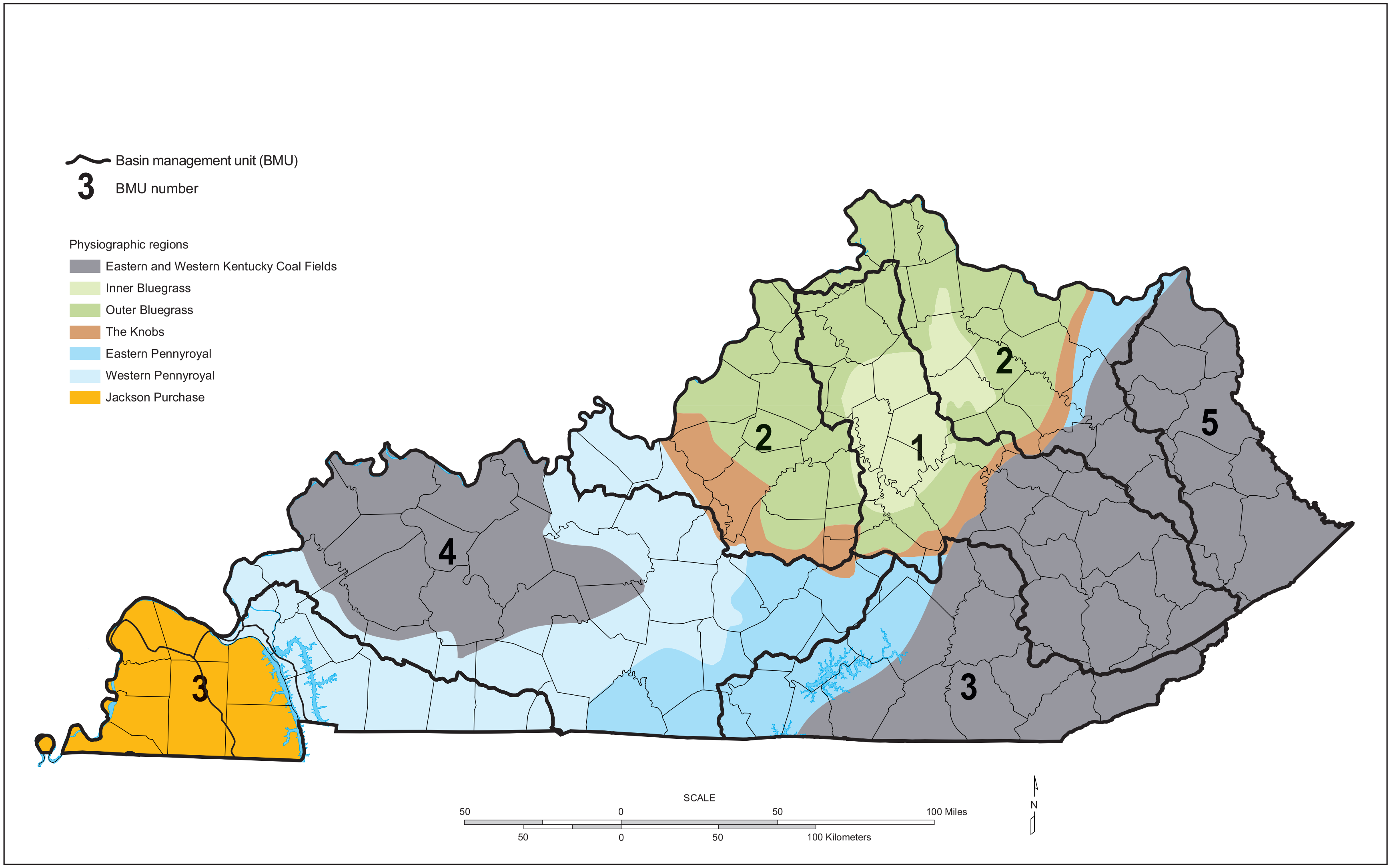

Figure 1. Physiographic regions, Basin Management Units, and major river watersheds in BMU 3.

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 Hydrologic 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 |
|---|---|
| **051301** | **Upper Cumberland River<br>(Eastern Kentucky Coal Field, Knobs, Eastern Pennyroyal)** |
| 05130101 | Upper Cumberland River |
| 05130102 | Rockcastle River |
| 05130103 | Cumberland River |
| 05130104 | South Fork Cumberland River |
| 05130105 | Dale Hollow Lake |
| **051302** | **Lower Cumberland River (Western Pennyroyal)** |
| 05130205 | Barkley Lake, Cumberland River |
| 05130206 | Lower Cumberland River, Red River |
| **051402** | **Ohio River Tributaries (Jackson Purchase)** |
| 05140206 | Ohio River, Massac Creek |
| **060400** | **Lower Tennessee River (Western Pennyroyal, Jackson Purchase)** |
| 06040005 | Tennessee River, Kentucky Lake |
| 06040006 | Tennessee River, Clarks River |
| **080101** | **Mississippi River Tributaries (Jackson Purchase)** |
| 08010100 | Mississippi River |
| **080102** | **Mayfield Creek, Obion Creek, Bayou de Chien, Mississippi River<br>(Jackson Purchase)** |
| 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 ($PO_4$-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).
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.

| | Parameter | Standard (mg/L unless otherwise noted) | Source |
|---|---|---|---|
| **Water Properties** | Conductance | 10,000 μS | 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 |
| **Inorganic Ions** | Sulfate | 250 | SMCL |
| | Fluoride | 4.0 | MCL |
| | Arsenic | 0.010 | MCL |
| | Barium | 2.0 | MCL |
| **Metals** | Iron | 0.3 | SMCL |
| | Manganese | 0.05 | SMCL |
| | Mercury | 0.002 | MCL |
| **Nutrients** | 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 |
| **Pesticides** | 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 |
| **Volatile Organic Compounds** | 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 wastersheds 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.

# Results

## Water Properties

**pH.** The property pH (negative base-10 logarithm of hydrogen ion activity in moles per liter) is one of the most fundamental water-quality parameters. It is easily measured, indicates whether water will be corrosive or will precipitate scale, determines the solubility and mobility of most dissolved constituents, and provides a good indication of the types of minerals groundwater has reacted with as it flows from recharge to discharge area or sample site.

The pH of neutral (neither acidic nor basic) water varies with temperature. For example, the neutral pH of pure water at 25°C (77°F) is 7.0. The neutral pH of pure water at 30°C (86°F) and 0°C (32°F) is 6.9 and 7.5, respectively (Hem, 1985). Solutes, including dissolved gases, also affect pH. Rain that has equilibrated with atmospheric carbon dioxide has a pH of about 5.6 (Hem, 1985). Streams and lakes in humid regions such as Kentucky typically have pH values between 6.5 and 8. Soil water in contact with decaying organic material can have values as low as 4, and the pH of water that has reacted with iron sulfide minerals in coal or shale can be even lower. In the absence of iron sulfide minerals, the pH of groundwater typically ranges from about 6.0 to 8.5, depending on the type of soil and rock contacted. Reactions between groundwater and sandstones result in pH values between about 6.5 and 7.5, whereas groundwater flowing through carbonate strata can have values as high as 8.5.

There are no health-based drinking water standards for pH. However, pH values outside of the range 6.5 to 8.5 can lead to high dissolved concentrations of some metals for which there are drinking water standards and associated health effects. The U.S. Environmental Protection Agency has established a secondary standard (SMCL) for pH of 6.5 to 8.5. Water with a pH value higher than 8.5 or lower than 6.5 can produce staining, etching, or scaling of equipment.

The data repository contained 2,589 pH values from 434 sites in BMU 3 (Table 4). The median pH value (6.9) is near neutral and the interquartile range is only 1.1 pH units. Few sites have pH values greater than 8.5, but many sites have pH values less than 6.5. Measured values follow a normal distribution between about 5.5 and 9.0 (Fig. 2).

There is a high density of sample sites in the Eastern Kentucky Coal Field portion of the Upper Cumberland River watershed, the eastern portion of the Lower Cumberland River watershed, and in the northern portion of the Tennessee River watershed (Fig. 3). Physiographic regions and the underlying rock types strongly influence pH values. Values range from less than 6.5 to greater than 8.5 in the geologically heterogeneous Eastern Kentucky Coal Field, are generally near neutral in the carbonate terrain of the Eastern and Western Pennyroyal Regions, and are commonly less than 6.5 in the sandy Jackson Purchase Region.

Comparing values within physiographic regions (Fig. 4) and major watersheds (Fig. 5) shows that bedrock geology, as represented by physiographic regions, is the primary control on groundwater pH. The Upper Cumberland River watershed includes parts of the Eastern Kentucky Coal Field and Eastern Pennyroyal Region. The highest and lowest pH values are found in the Eastern Kentucky Coal Field portion of the Upper Cumberland watershed, whereas samples from the Eastern Pennyroyal Region of the Upper Cumberland watershed have a smaller range of pH values and a higher median value than samples from the Eastern Kentucky Coal Field. Samples from the Lower Cumberland watershed (entirely within the Western Pennyroyal Region) and the Ohio and Mississippi watersheds (entirely within the Jackson Purchase Region) have a relatively small range of values, reflecting the geologic

**Table 4.** Summary of pH values (standard pH units).

| | |
|---|---|
| Measurements | 2,589 |
| Maximum | 9.5 |
| 75th percentile | 7.4 |
| Median | 6.9 |
| 25th percentile | 6.3 |
| Minimum | 1.7 |
| Interquartile range | 6.3–7.4 |
| Sites | 434 |
| SMCL | 6.5–8.5 |
| Sites > 8.5 | 9 |
| Sites < 6.5 | 188 |

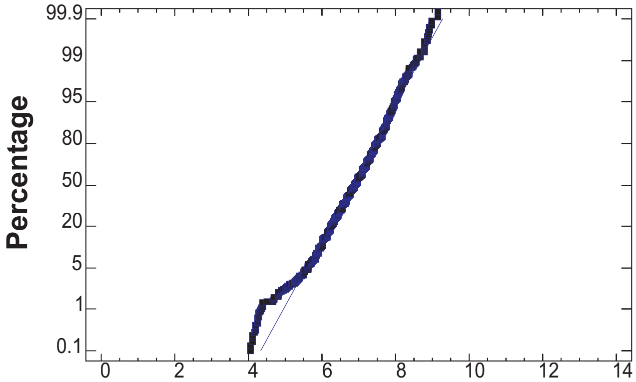

Figure 2. Cumulative plot of pH values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

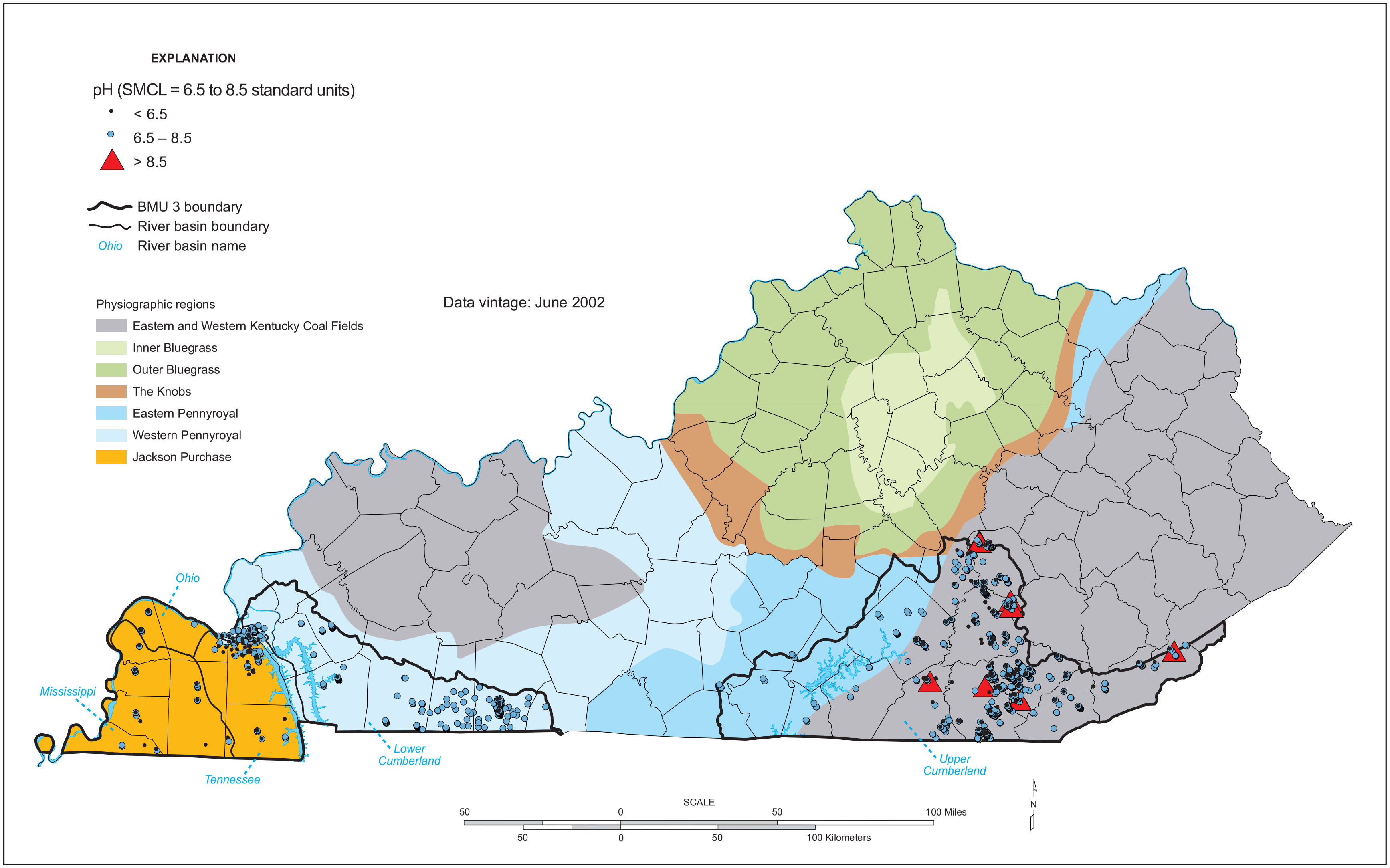

Figure 3. Sampled sites and ranges of pH values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

similarity within regions. Samples from the Tennessee River watershed have an interquartile range nearly as large as samples from the Upper Cumberland River watershed, because the Tennessee River watershed includes both the carbonate Western Pennyroyal Region and the sandy Jackson Purchase Region.

The interquartile range of pH values for both wells and springs is about one pH unit, although the total range of values is greater in wells than in springs (Fig. 6). The median pH value from springs is slightly higher than that from wells, because most springs are in carbonate terrain. Shallow wells have greater variability in pH than wells deeper than about 100 ft (Fig. 7).

In summary, groundwater pH values and ranges of values are more closely related to physiographic region than to major watershed. There is no unequivocal evidence of widespread nonpoint-source contamination. Groundwater in the predominantly carbonate-rich geology of the Eastern and Western Pennyroyal Regions is nearly neutral, and pH values show relatively little variability. In the Eastern Kentucky Coal Field, where bedrock lithology is more heterogeneous, groundwater pH shows a much wider range of values. Groundwater in the sandy Jackson Purchase, where carbonate minerals are scarce, is generally slightly acidic. The pH of springs and shallow wells is much more variable than the pH of water from intermediate and deep wells. The decrease in variability of pH with sample depth shows that groundwater in intermediate and deep flow systems has equilibrated with bedrock to a greater extent than groundwater in springs and shallow wells.

A statewide summary of pH data (Fisher, 2002b) can be viewed on the Kentucky Geological Survey Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

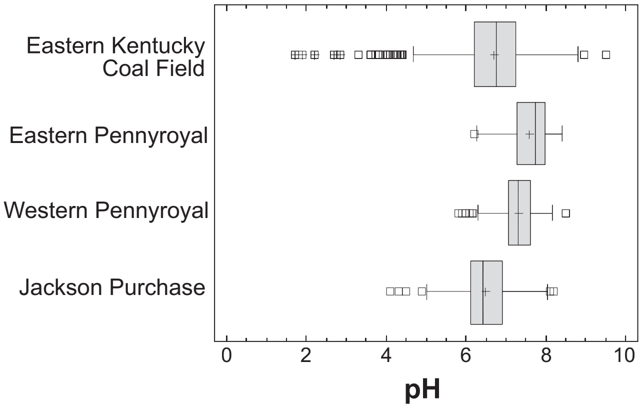

Figure 4. Summary of pH values grouped by physiographic region.

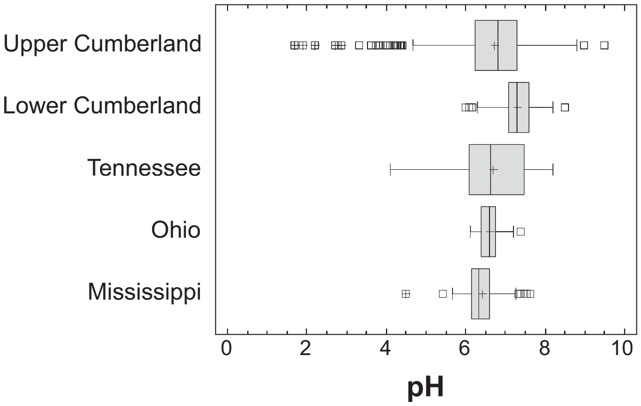

Figure 5. Summary of pH values grouped by major watershed.

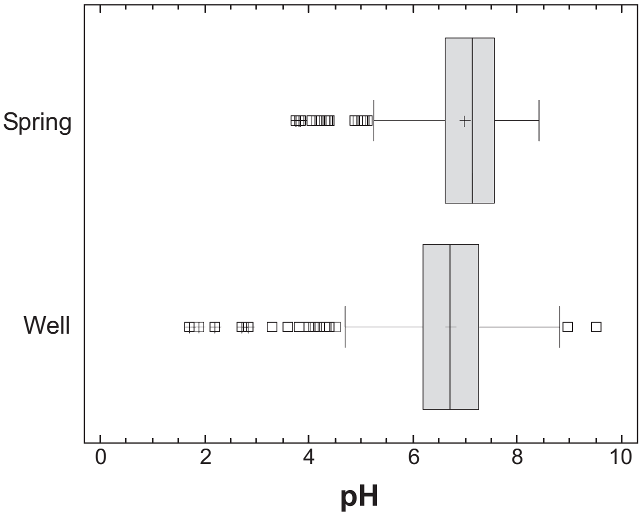

Figure 6. Comparison of pH values from wells and springs.

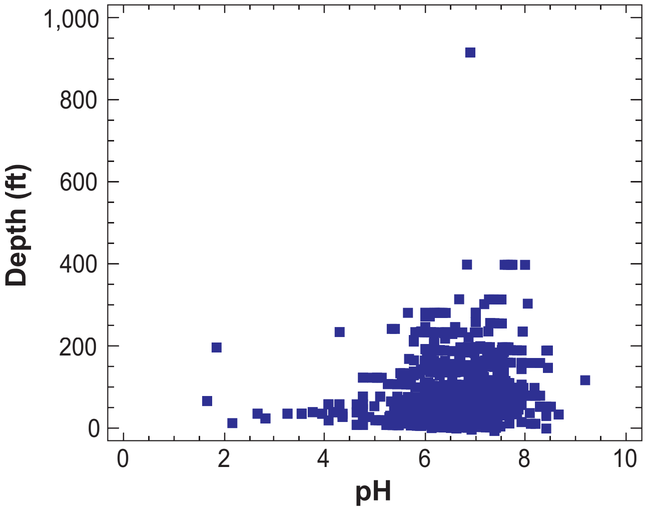

Figure 7. Plot of pH values versus well depth.

**Total Dissolved Solids.** Total dissolved solids is reported as the sum of all dissolved chemicals in water expressed as mg/L. TDS can be calculated by adding all the solute concentrations from a complete chemical analysis or measured as the weight of the residue remaining after a known volume of water has been evaporated to dryness.

TDS values are a general indicator of the suitability of groundwater for various uses (Mazor, 1991, p. 94–95):

*Potable water:* up to 500 mg/L TDS
*Slightly saline water:* adequate for drinking and irrigation (500 to 1,000 mg/L TDS)
*Medium saline water:* potable only in cases of need; may be used for some crops and aquiculture (1,000 to 2,500 mg/L TDS)
*Saline water:* adequate for aquiculture and industrial use (2,500 to 5,000 mg/L TDS)
*Brackish water:* 5,000 to 35,000 mg/L TDS (the salinity of seawater)
*Brine:* TDS greater than 35,000 mg/L

The EPA has set an SMCL of 500 mg/L TDS. Water having values greater than 500 mg/L has an unpleasant taste and may stain objects or precipitate scale in containers, plumbing, or water heaters.

The Kentucky Groundwater Data Repository contained 632 reports of TDS at 150 sites in BMU 3. Total dissolved solids measurements are summarized in terms of suitability for various uses (Table 5). Nearly all samples and sites yielded potable water. Only three measurements exceeded 2,500 mg/L; no measurements exceeded 5,000 mg/L. A cumulative data plot (Fig. 8) shows that TDS values below about 400 mg/L follow a normal distribution.

TDS values were reported at relatively few sites, and those locations are evenly distributed throughout the project area (Fig. 9). Potable water is present throughout the area. A summary of data grouped by physiographic region (Fig. 10) shows that groundwater in the Eastern Pennyroyal has the smallest range of values, whereas samples from the Western Pennyroyal have the greatest variability of TDS values. The highest values occur in the Lower Cumberland River watershed, whereas sites in the Tennessee River watershed have the smallest range of values (Fig. 11).

Although springs and wells have approximately the same median TDS value and a similar interquartile range (Fig. 12), the highest TDS values are found in wells. Deeper wells have somewhat lower TDS values than shallow wells (Fig. 13).

In summary, nearly 95 percent of the reported TDS values in the project area are less than 500 mg/L. Values greater than 500 mg/L are found in all major watersheds and all regions except the Eastern Pennyroyal. Some high TDS values in the Eastern Kentucky Coal Field may represent groundwater discharge from deep, regional flow systems (Wunsch, 1993). High TDS values in the Western Pennyroyal Region may be naturally occurring (Hopkins, 1966) or caused by brines from nearby oil and gas production wells. Slightly saline to medium saline groundwater in the Jackson Purchase Region probably indicates that samples came from deeper wells than the potable water.

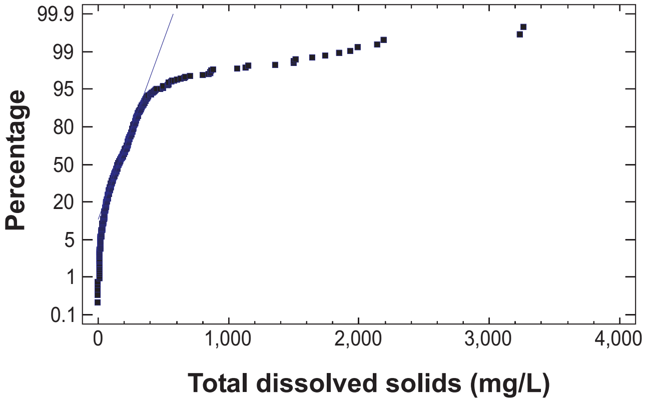

Figure 8. Cumulative plot of total dissolved solids values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

**Table 5.** Summary of total dissolved solids values (mg/L).

| Total Dissolved Solids (mg/L) | Percentage of Analyses | Percentage of Analyses |
|---|---|---|
| Potable water (0–500) | 94 | 87 |
| Slightly saline (501–1,000) | 3 | 7 |
| Medium saline (1,001–2,500) | 3 | 5 |
| Saline: (2,501–5,000) | < 1 | < 1 |
| Brackish: (5,001–35,000) | 0 | 0 |
| Brine: (> 35,000) | 0 | 0 |

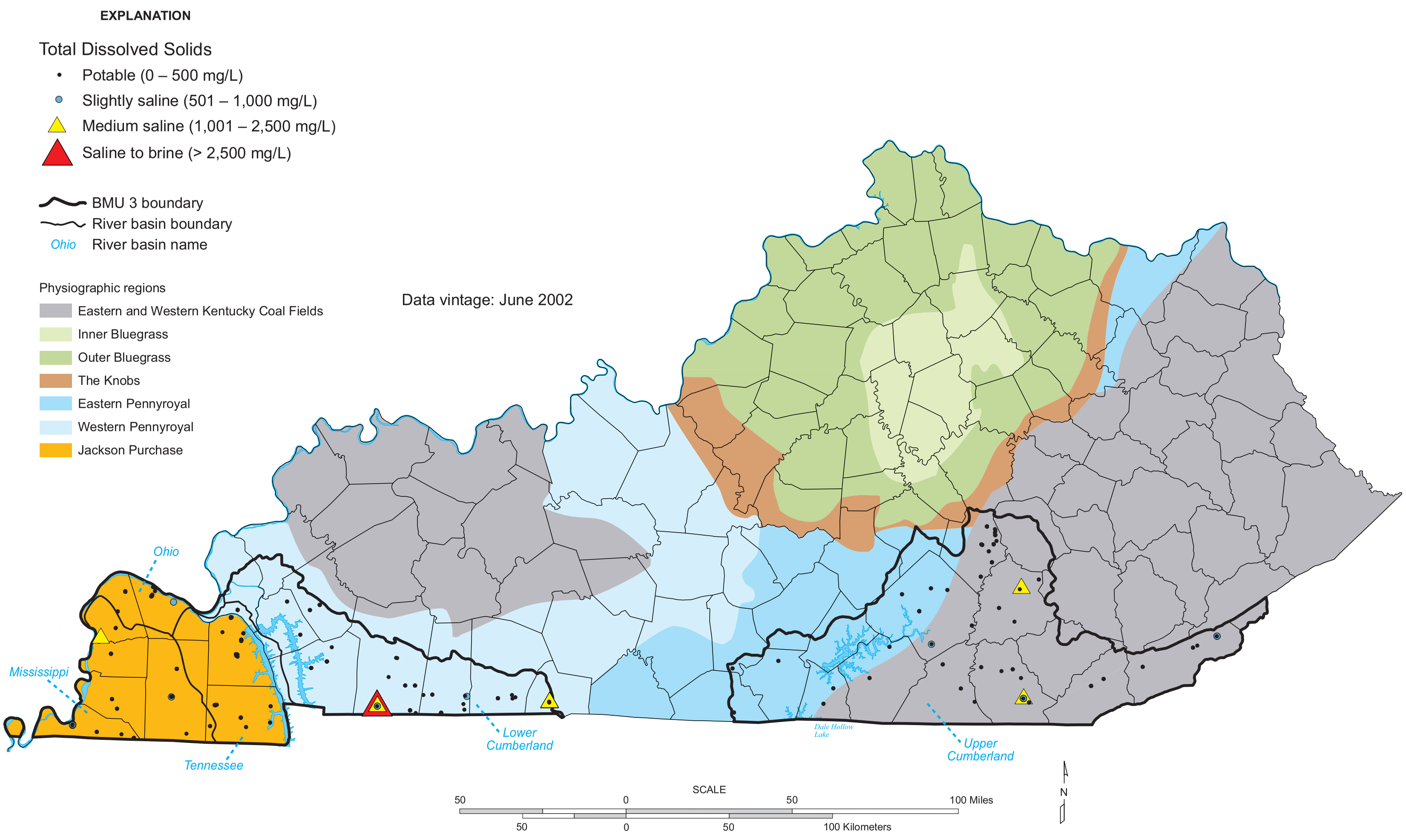

Figure 9. Sample sites and ranges of total dissolved solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

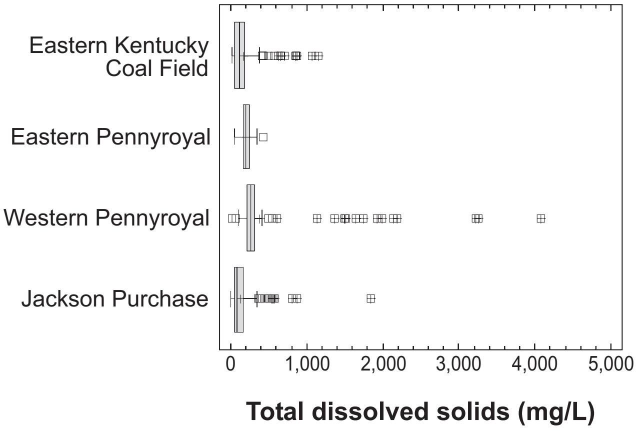

Figure 10. Summary of total dissolved solids values grouped by physiographic region.

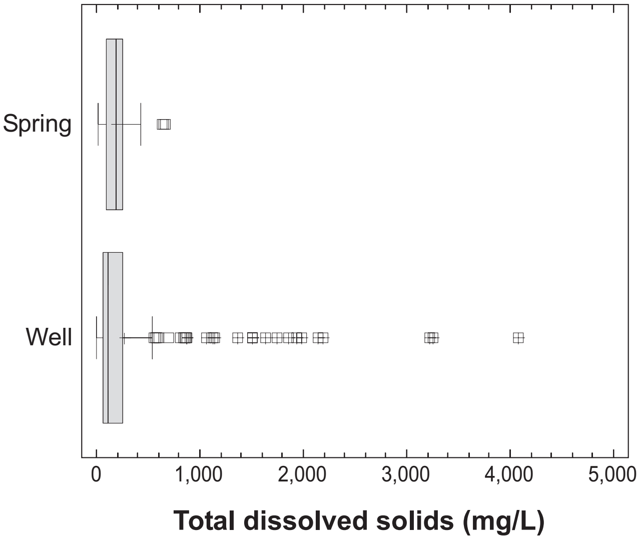

Figure 12. Comparison of total dissolved solids values from wells and springs.

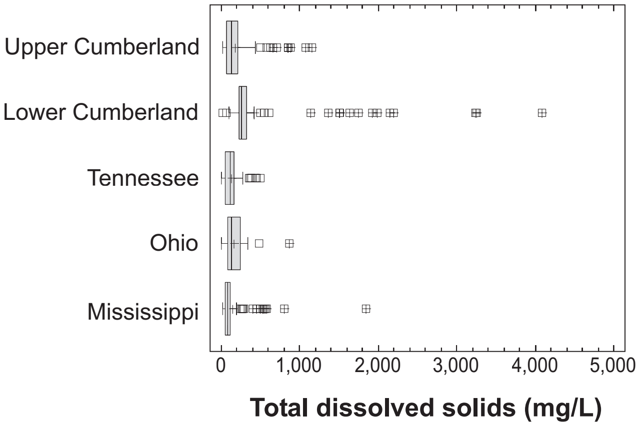

Figure 11. Summary of total dissolved solids values grouped by major watershed.

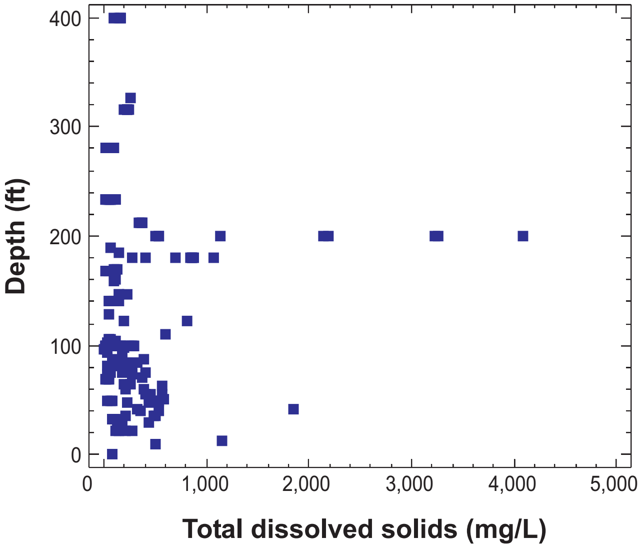

Figure 13. Total dissolved solids values versus well depth.

**Specific Electrical Conductance.** Specific electrical conductance, also referred to as conductivity, is a measure of the ability of water to conduct an electrical current. It is proportional to total dissolved solids concentrations and therefore an indirect measure of water quality. Specific electrical conductance is a quick and simple measurement to make in the field, and provides a relative comparison of water quality if the samples being compared have nearly the same temperature and predominant cations and anions (for example, sodium and chloride or calcium and bicarbonate).

Conductance is reported in micromhos per centimeter at 25°C, or the numerically equivalent microSiemens per centimeter (µS/cm) in the International System of Units (Hem, 1985). Because conductance does not directly indicate water quality, there are no health or water-use standards based on this parameter.

The data repository contained a large number of conductance measurements in BMU 3 as a result of the extensive sampling program associated with the National Uranium Resource Evaluation project (Smith, 2001). Well depths range to 4,100 ft. Samples from depths greater than 730 ft were collected and reported as part of a USGS program that surveyed water quality in accessible wells throughout Kentucky. Although identified as water wells, samples from such depths do not represent the part of the groundwater system that would be used by private citizens. The deepest sample reported by the Division of Water and identified as a water well was 730 ft. Therefore, to exclude data from exploration wells or oil and gas wells that were incorrectly labeled water wells, we excluded conductance values from depths greater than 730 ft from this summary. The resulting data set is summarized in Table 6 and Figure 14. Less then 5 percent of the measurements exceeded 500 µS/cm; however, values as high as 178,000 µS/cm have been reported.

**Table 6.** Summary of conductance values (µ/cm).

| | |
|---|---|
| Measurements | 5,308 |
| Maximum | 178,000 |
| 75th percentile | 410 |
| Median | 269 |
| 25th percentile | 128 |
| Minimum | 3.4 |
| Interquartile range | 128–410 |
| Sites | 3,430 |

Sample coverage is dense throughout BMU 3 (Fig. 15) and a general absence of values greater than 10,000 µS/cm in the Lower Cumberland, Tennessee, Ohio, and Mississippi River watersheds. Most conductance values greater than 10,000 µS/cm are found at sites in the southwestern part of the Upper Cumberland River watershed.

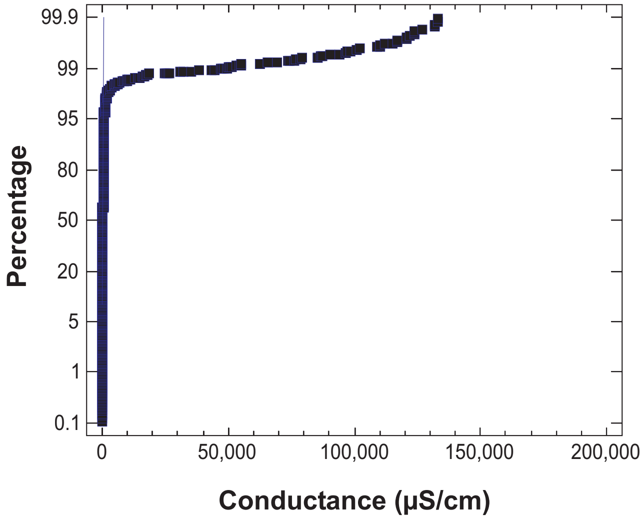

Figure 14. Cumulative plot of conductance values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Grouping the data by physiographic region (Fig. 16) and by major river watershed (Fig. 17) shows that, with only one exception, values exceeding 10,000 µS/cm are from sites in the Eastern Kentucky Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland River watershed. The exception is one measured value from a site in the Western Pennyroyal Region of the Lower Cumberland River watershed.

The highest values are found in wells rather than springs (Fig. 18).

Although there are many outlier values, conductance generally decreases with well depth (Fig. 19).

In summary, more than 95 percent of the reported conductance values are less than 500 µS/cm. Values higher than 10,000 µS/cm are found in groundwater from wells in the Eastern Kentucky Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland watershed. Nearly all of these high conductance values were reported as part of a regional groundwater-quality survey conducted by the U.S. Geological Survey during the 1960's and 1970. Few well depths were reported; however, four wells having depths less than 100 ft yielded groundwater with conductance above 10,000 µS/cm. Although there is no way to confirm the very high conductance values, there is also no reason to assume they do not accurately represent the sampled sites. Some high values in the Eastern Kentucky Coal Field may represent discharge of deep, naturally brackish groundwater, and some high values in the Eastern Pennyroyal may represent nonpoint-source contamination from abandoned oil and gas wells.

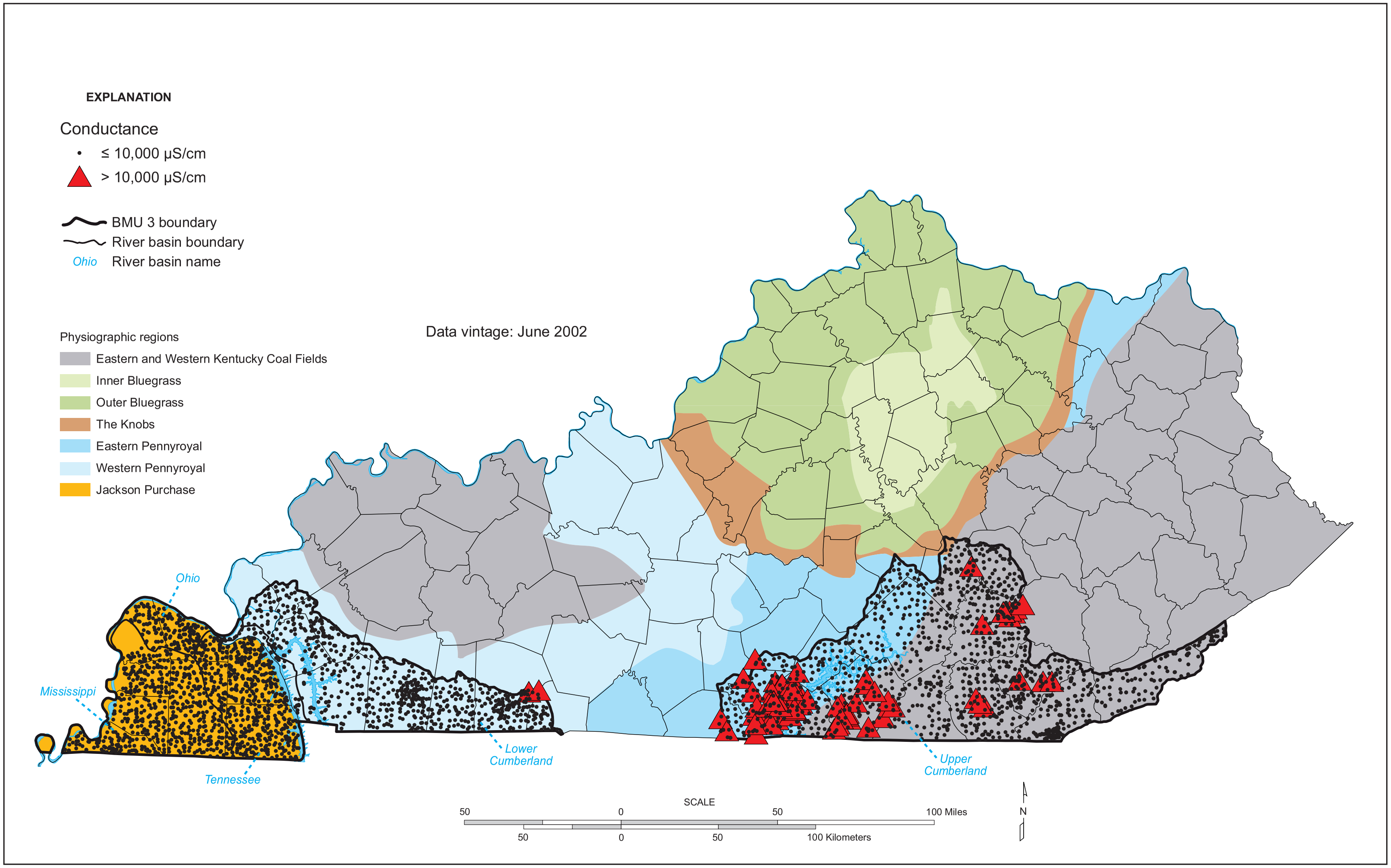

Figure 15. Sample sites and ranges of conductance values.

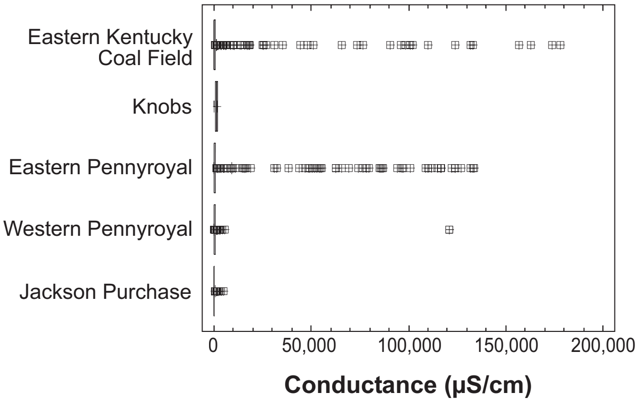

Figure 16. Summary of conductance values grouped by physiographic region

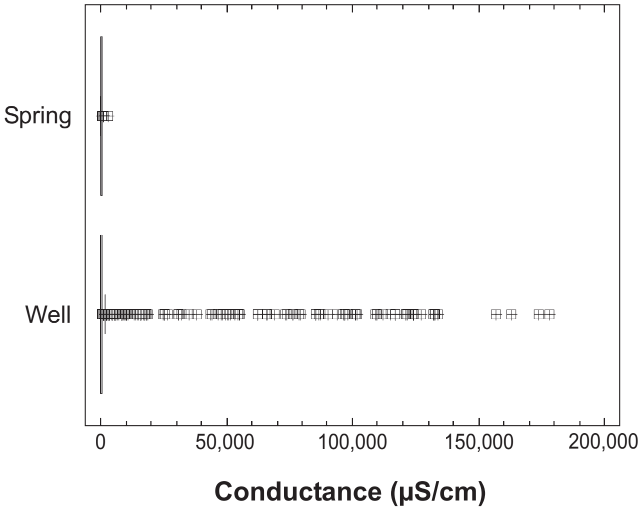

Figure 18. Comparison of conductance values from wells and springs.

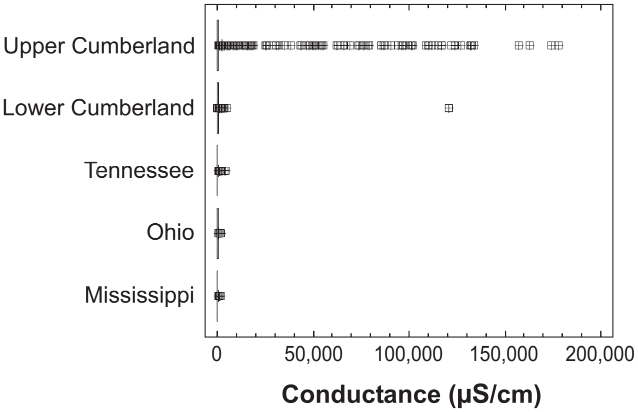

Figure 17. Summary of conductance values grouped by major river watershed.

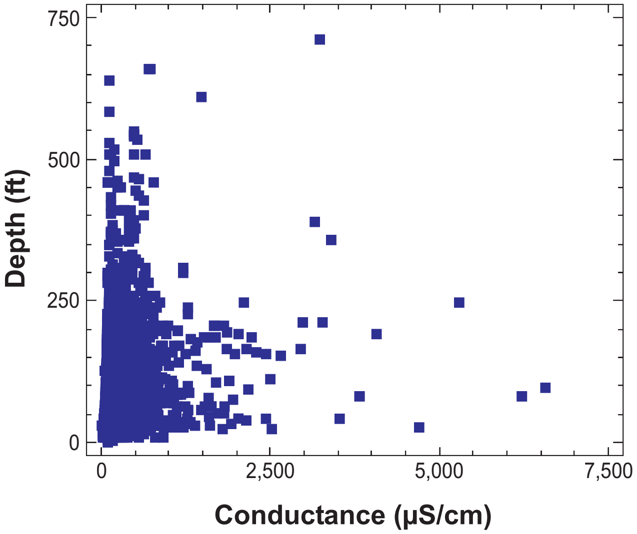

Figure 19. Conductance versus well depth. Higher conductance values have been omitted to better show the main trend of data.

**Hardness.** Hardness refers to the tendency of water to precipitate an insoluble residue when soap is used, and to form a scale on containers when water evaporates. Hard water reduces the ability of soap and detergents to clean clothes; leaves a sticky film on skin, clothes, and hair; and deposits scale in water heaters, boilers, and industrial equipment.

Because calcium and magnesium are largely responsible for the behavior of soap in water, hardness is usually defined as the concentrations of calcium and magnesium expressed as an equivalent amount of calcium carbonate:

Hardness (mg/L calcium carbonate equivalent) = 2.5 Ca (mg/L) + 4.1 Mg (mg/L).

A frequently used classification of hardness in water supplies is shown in Table 7 (U.S. Geological Survey, 2006).

**Table 7.** Hardness classification of water supplies.

| Hardness Category | Concentration (mg/L) |
|---|---|
| Soft | 0–17 |
| Slightly hard | 18–60 |
| Moderately hard | 61–120 |
| Hard | 121–180 |
| Very hard | > 180 |

Calcium and magnesium concentrations from the data repository were combined according to the above equation to produce 1,942 groundwater hardness values at 649 sites in BMU 3 (Table 8). Less than 50 percent of the values represent soft to moderately hard water, whereas 44 percent of the samples represent very hard water.

**Table 8.** Summary of hardness values (mg/L).

| | |
|---|---|
| Measurements | 1,942 |
| Maximum | 130,072 |
| 75th percentile | 242 |
| Median | 131 |
| 25th percentile | 40 |
| Minimum | 0.3 |
| Sites | 649 |
| Sites < 17 (soft water) | 78 |
| Sites 18–60 (slightly hard water) | 130 |
| Sites 61–120 (moderately hard water) | 73 |
| Sites 121–180 (hard water) | 81 |
| Sites > 180 (very hard water) | 287 |

The lower 85 percent of values follows a normal distribution, with excursions to very high values in the remaining 15 percent (Fig. 20).

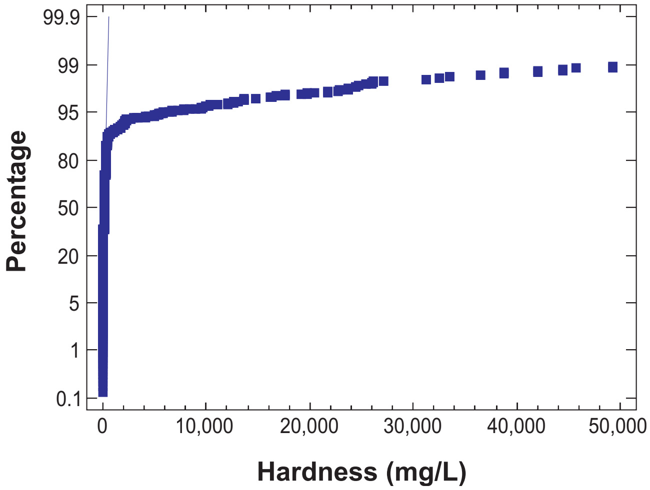

Figure 20. Cumulative plot of hardness values. Values greater than 50,000 mg/L have been omitted to better show the majority of the data.

Sample distribution is dense in all areas except the northern part of the Upper Cumberland River watershed (Fig. 21). Water is soft to moderately hard in the Jackson Purchase Region, hard to very hard in the Eastern and Western Pennyroyal Regions, and highly variable in the Eastern Kentucky Coal Field (Figs. 21–22).

Samples from the Lower Cumberland, Tennessee, Ohio, and Mississippi River watersheds have a small range of values (Fig. 23) because sites in those watersheds are in geologically homogeneous terrain. Samples from the Upper Cumberland watershed have a very large range of values because of the geologic heterogeneity of the Eastern Kentucky Coal Field.

The highest hardness values are found in groundwater from wells rather than from springs (Fig. 24). There is a general trend of decreasing hardness with depth in water wells (Fig. 25).

In summary, hard to very hard groundwater is predominant throughout the project area, with the exception of water from wells in the sandy Jackson Purchase Region. In both the Eastern Kentucky Coal Field and the Eastern Pennyroyal carbonate terrain, dissolved calcium and magnesium supplied by calcite and dolomite produce hard water. These minerals are absent or present only in low abundance in the gravels, sands, silts, and clays of the Jackson Purchase Region. Very high hardness values in the Eastern Kentucky Coal Field may be the result of acidic groundwater dissolving carbonate minerals and producing high calcium and magnesium concentrations.

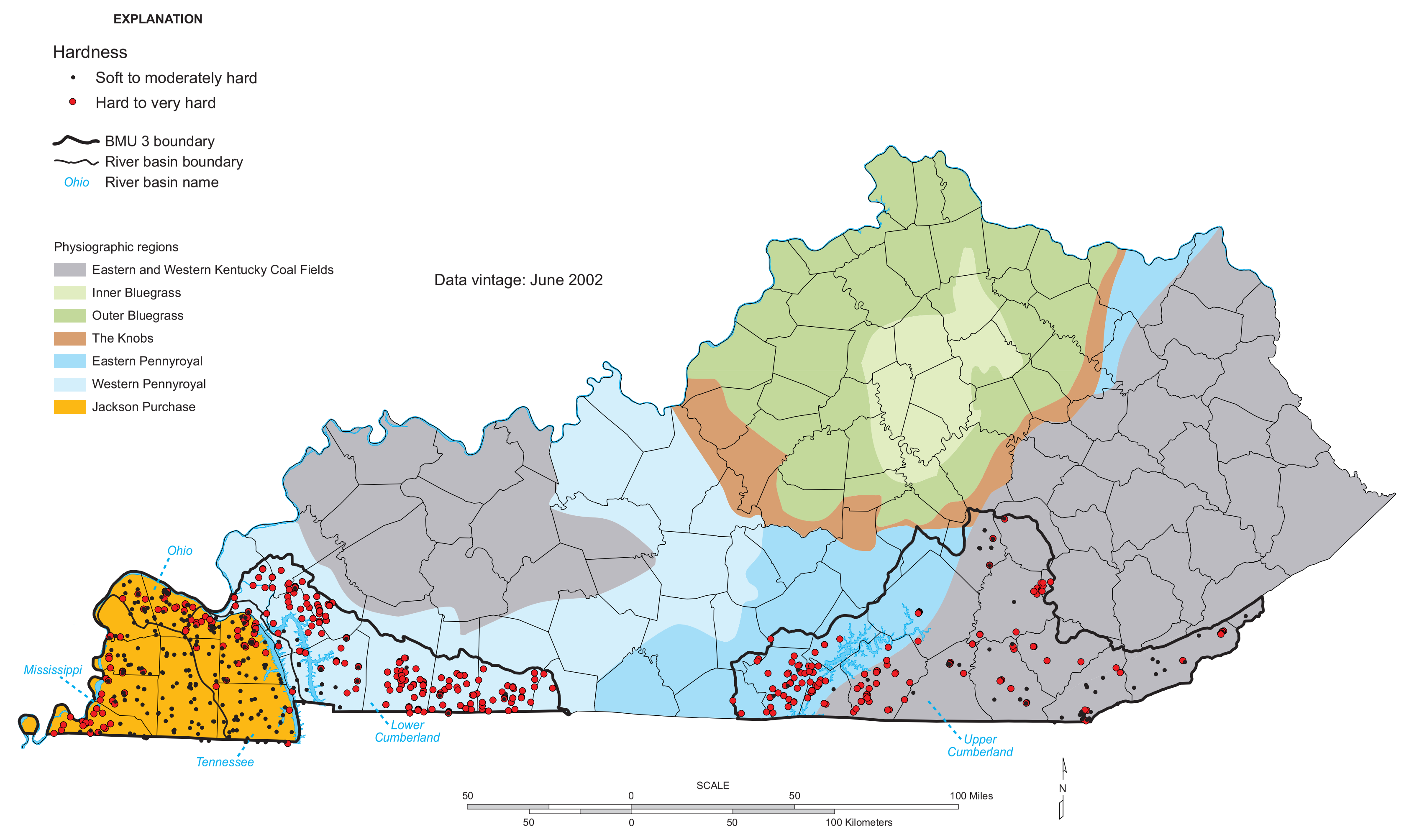

Figure 21. Sample sites and ranges of hardness values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

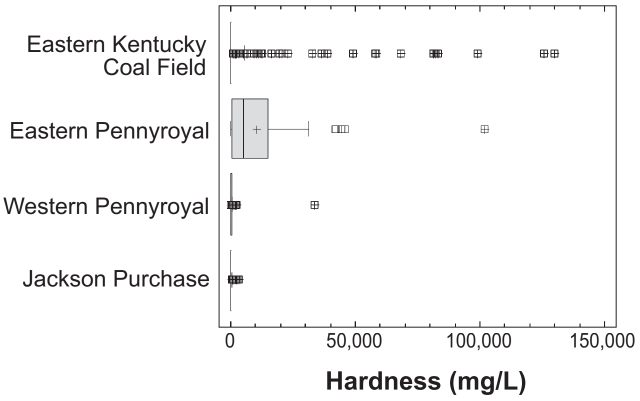

Figure 22. Summary of hardness values grouped by physiographic region.

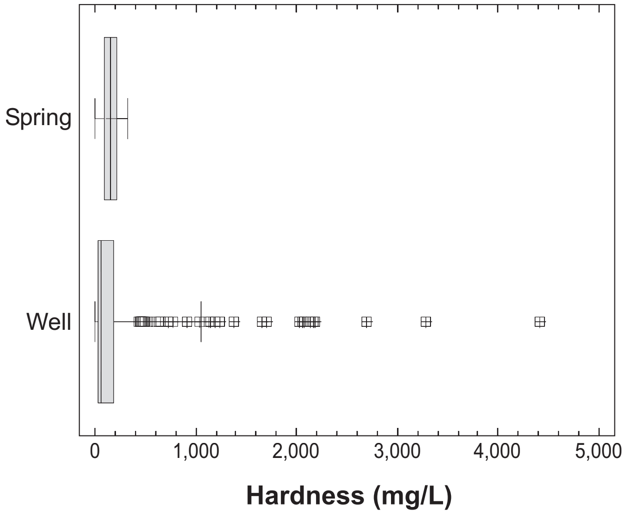

Figure 24. Comparison of hardness values from wells and springs. Higher values were omitted to better show the similarity in interquartile ranges.

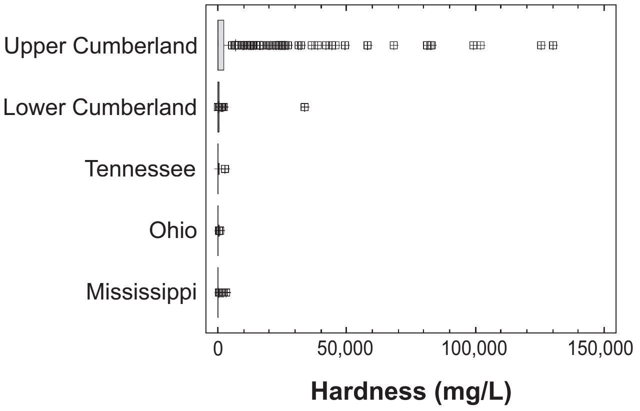

Figure 23. Summary of hardness values grouped by major river watershed.

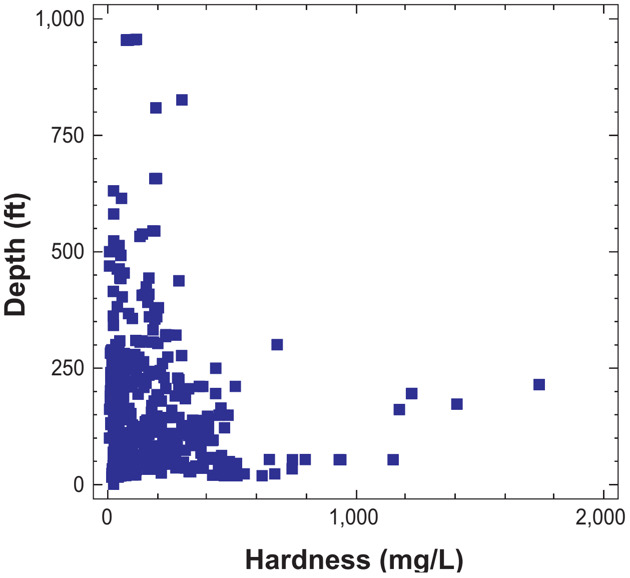

Figure 25. Hardness values versus well depth. Higher values were omitted to better show the majority of the data points.

**Total Suspended Solids.** Suspended particulate material is reported as total suspended solids. TSS values are typically higher in samples from karst springs or wells in fractured aquifers, where turbulent flow can transport fine material such as clays and particulate organic material, and from uncased wells that have been vigorously stirred during purging prior to sample collection than in water from wells in granular bedrock. TSS measurements also include any precipitate that formed in the sample bottle after collection.

There are no health or cosmetic standards for total suspended solids in water. Some metals and pesticides are preferentially sorbed onto or included in the matrix of suspended material, however, so water high in total suspended solids may also contain significant amounts of metals that may have health or safety implications. Also, high amounts of suspended material can clog plumbing systems and stain clothing and water containers. The Kentucky Pollution Discharge Elimination System recommends that total suspended solids levels be less than 35 mg/L.

In BMU 3 there are 622 measurements of total suspended solids from 109 sites. The values range from 0 to 442 mg/L (Table 9). Despite the high maximum value, the median and interquartile range of total suspended solids values are very low. Eighty percent of the total suspended solids measurements are less than 10 mg/L and 90 percent are less than 20 mg/L (Fig. 26).

**Table 9.** Summary of total suspended solids values (mg/L).

| | |
|---|---|
| Measurements | 622 |
| Maximum | 442 |
| 75th percentile | 4 |
| Median | 3 |
| 25th percentile | 3 |
| Minimum | 0 |
| Interquartile range | 3–4 |
| Sites | 109 |
| DOW recommended value | 35 |
| Sites > 35 | 14 |

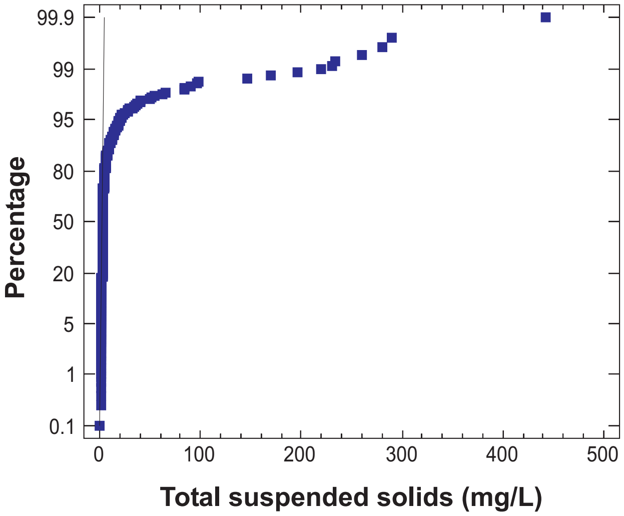

Figure 26. Cumulative plot of total suspended solids values.

Sample site distribution is rather uniform throughout the project area (Fig. 27).

The highest total suspended solids values are found In the Ohio and Tennessee River watersheds in the Jackson Purchase Region (Figs. 28–29). Although many high values are reported from the Jackson Purchase (Fig. 28), they are from only two sites (Fig. 27). Values from sites in the Mississippi River watershed are uniformly low (Fig. 29).

The highest total suspended solids values are reported from wells rather than springs (Fig. 30); wells less than 100 ft deep have the highest total suspended solids values (Fig. 31).

In summary, suspended solids may be locally derived as a result of vigorous well purging before sampling or may be transported by turbulent groundwater flow. Total suspended solids concentrations can be significant because suspended clays and organic material preferentially carry some potentially toxic metals and synthetic organic chemicals. The distribution of the highest total suspended solids values suggests that springs in the Western Pennyroyal Region carry significant amounts of suspended material, and that suspended sediment concentrations are also high in a few wells in the generally unconsolidated to poorly consolidated sands, silts, and clays in the Jackson Purchase Region.

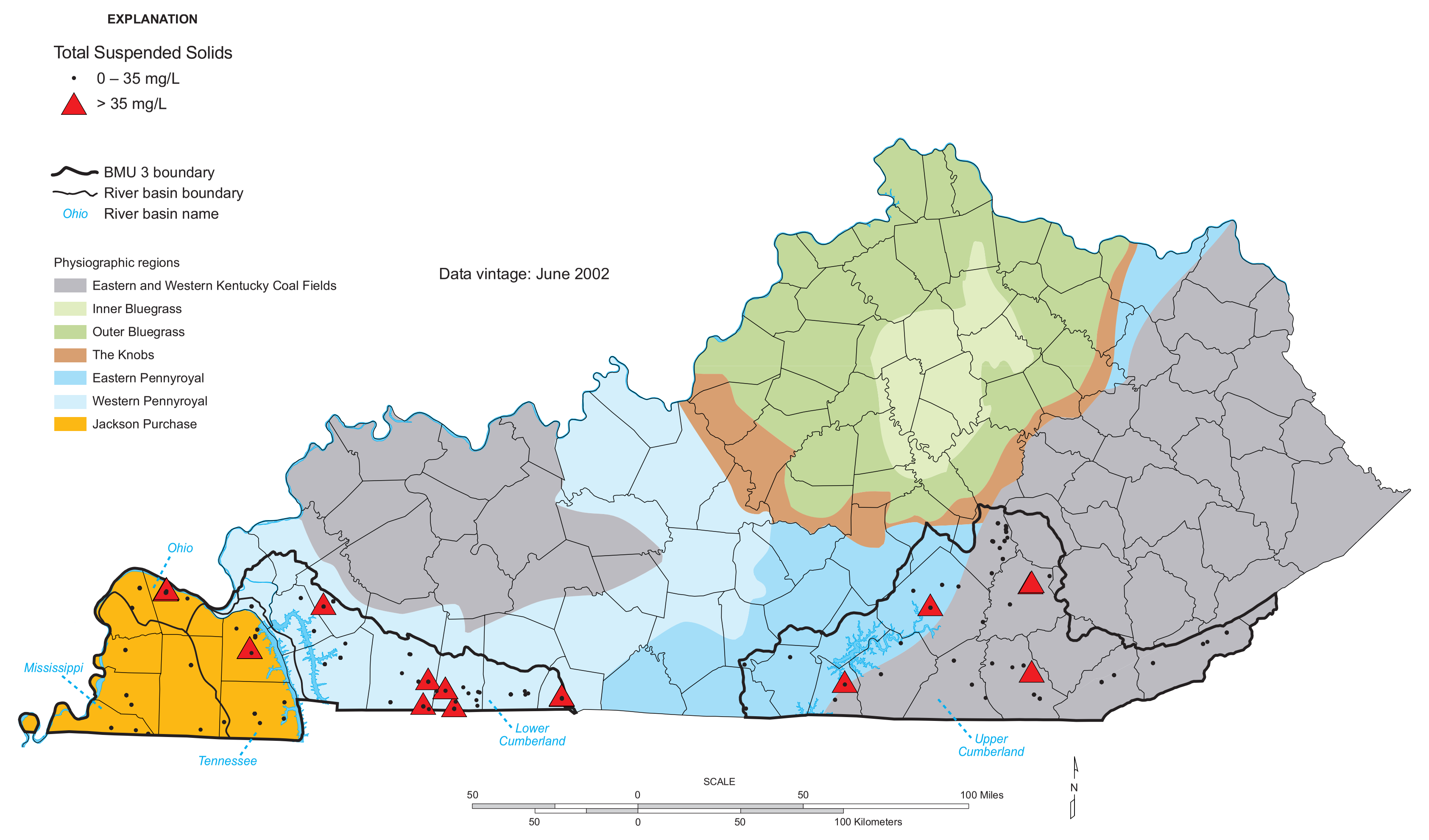

Figure 27. Sample sites and ranges of total suspended solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

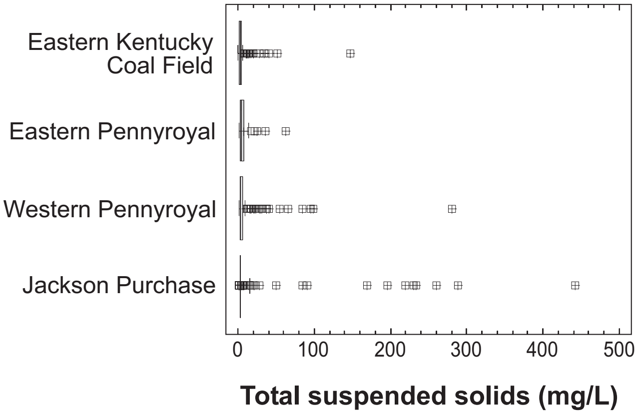

Figure 28. Summary of total suspended solids values grouped by physiographic region.

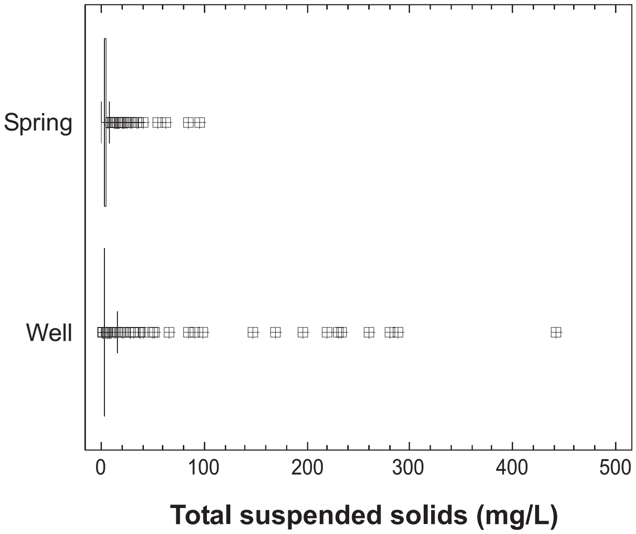

Figure 30. Comparison of total suspended solids values from wells and springs.

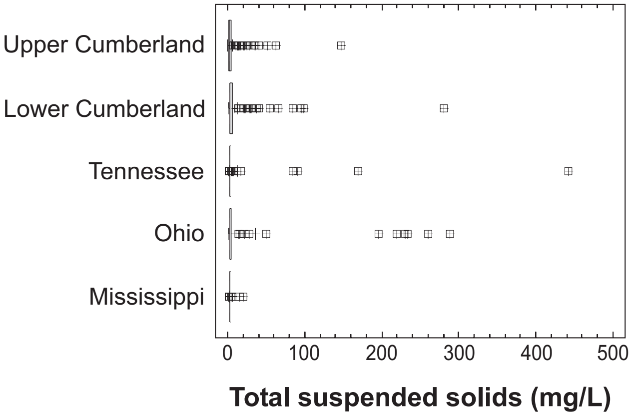

Figure 29. Summary of total suspended solids values grouped by major watershed.

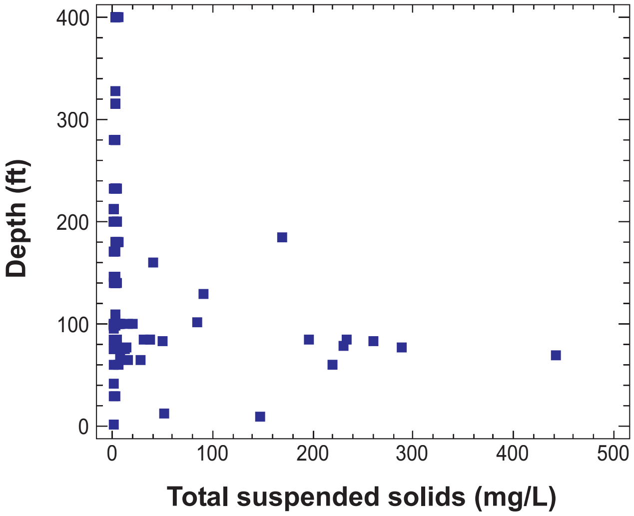

Figure 31. Total suspended solids values versus well depth.

## Inorganic Anions

**Chloride.** Chloride (Cl) is present in most natural groundwater in low to moderate amounts. It is a highly conservative anion, meaning once in solution it is not involved in oxidation/reduction reactions, does not form complexes with other major ions or precipitate out as low-solubility minerals, and is not readily sorbed onto the aquifer matrix. In Kentucky groundwater, the main sources of chloride are interstitial fluids in shales and brackish groundwater that is commonly encountered at depth in the coal fields and the Pennyroyal Region (Hopkins, 1966; Wunsch, 1993). Nonpoint sources include contamination from oil or gas wells, road salt, confined animal feeding operations, and defective septic waste-disposal systems.

There are no health-related standards for chloride. The EPA has set a secondary maximum contaminant level of 250 mg/L for chloride because water containing more than this amount has an unpleasant taste that makes it unsuitable for domestic use.

Chloride concentrations from wells as deep as 4,200 ft have been reported. As with the conductance data discussed previously, chloride results from wells deeper than 730 ft were excluded from this data summary because they are not part of the groundwater system that could be used by citizens or municipalities for water supplies. The resulting data set is summarized in Table 10. Although chloride concentrations as high as 130,000 mg/L occur in the project area, more than 96 percent of the samples in BMU 3 contain less than 250 mg/L chloride. Seventy-five percent of the reported values are less than 12 mg/L.

**Table 10.** Summary of chloride values (mg/L).

| | |
|---|---|
| Measurements | 7,542 |
| Maximum | 130,000 |
| 75th percentile | 11.6 |
| Median | 5.8 |
| 25th percentile | 3.0 |
| Minimum | 0.0 |
| Interquartile range | 3.0–11.6 |
| Sites | 3,513 |
| SMCL | 250 |
| Sites > 250 | 133 |

There is a sharp break in the distribution of chloride values at about 250 mg/L (Fig. 32). Chloride concentrations less than about 250 mg/L follow a normal distribution.

Chloride concentrations were reported for a very large number of sites distributed throughout the area (Fig. 33). Sites having chloride concentrations greater than 250 mg/L are most common in the southwestern part of the Eastern Pennyroyal and Eastern Kentucky Coal Field Regions of the Upper Cumberland watershed.

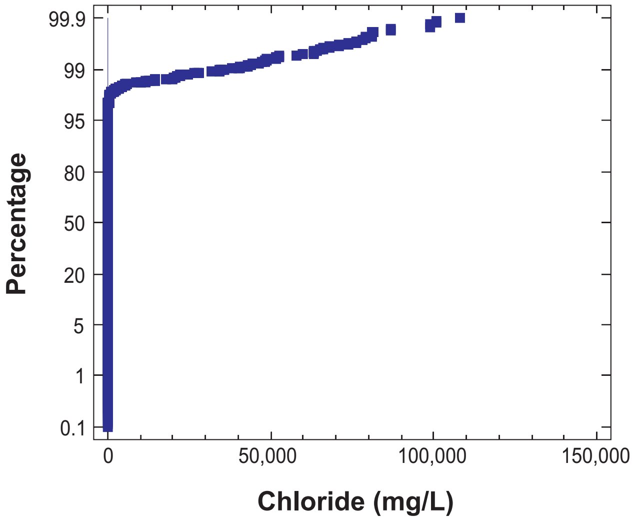

Figure 32. Cumulative plot of chloride values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Chloride concentrations greater than 10,000 mg/L are common only in the Eastern Kentucky Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland River watershed (Figs. 34–35). Chloride concentrations in other physiographic regions and major watersheds are generally low.

Groundwater from wells is more likely to have very high chloride concentrations than groundwater from springs (Fig. 36). The highest chloride concentrations are found in wells that are less than 200 ft deep (Fig. 37). At well depths greater than about 250 ft, chloride concentrations are generally less than 100 mg/L.

In summary, more than 96 percent of the reported chloride concentrations are less than 250 mg/L throughout the project area. Sites that produce groundwater that exceeds this level are found primarily in the Eastern Pennyroyal and Eastern Kentucky Coal Field Regions of the Upper Cumberland River watershed. High chlorinity is more common in water from wells than from springs, and more common in wells less than about 250 ft deep than in deeper wells. Chloride values exceeding 100,000 mg/L have been reported from wells that are less than 730 ft deep and from wells for which depth was not reported. These samples may be from sites that are contaminated from leaking oil or gas wells or by other nonpoint sources; further investigations are needed to determine the source of the chlorinity at each site.

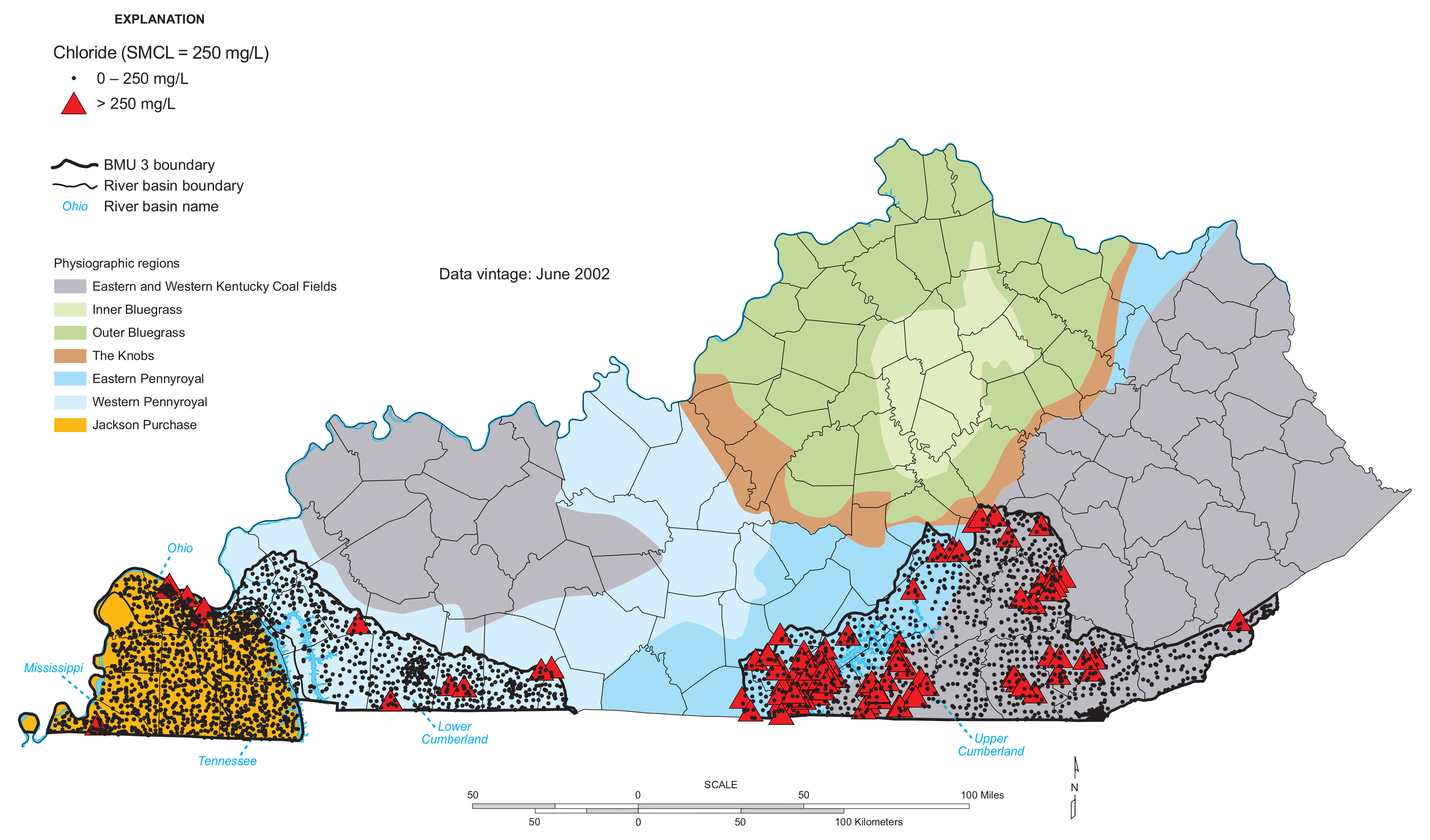

Figure 33. Sample sites and ranges of chloride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

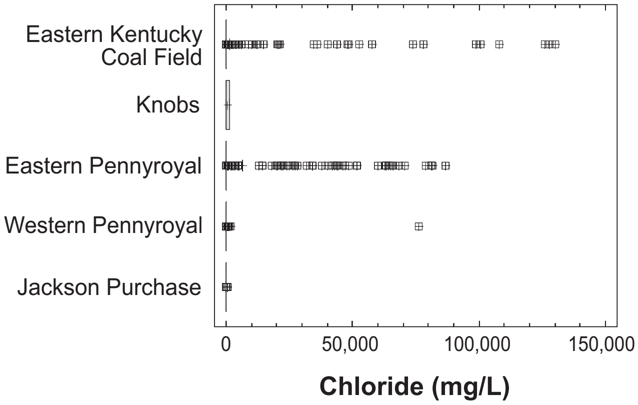

Figure 34. Summary of chloride values grouped by physiographic region.

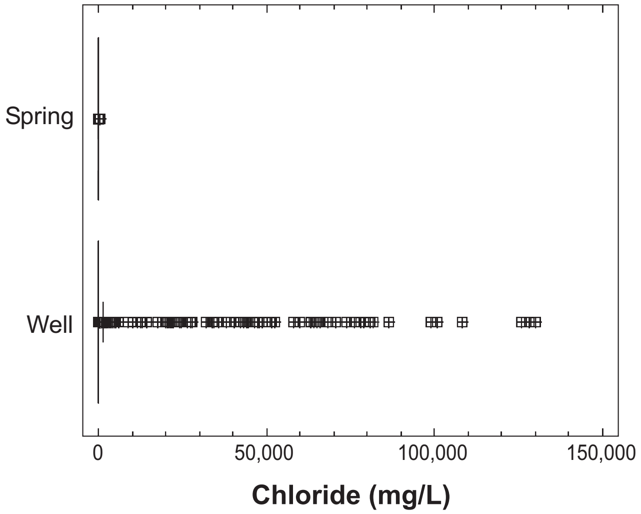

Figure 36. Comparison of chloride values from wells and springs.

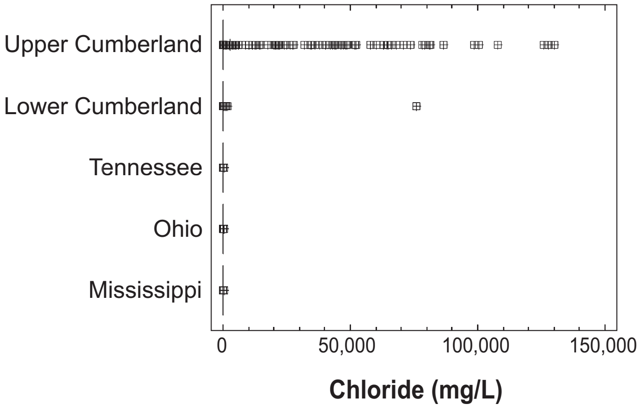

Figure 35. Summary of chloride concentrations grouped by major watersheds.

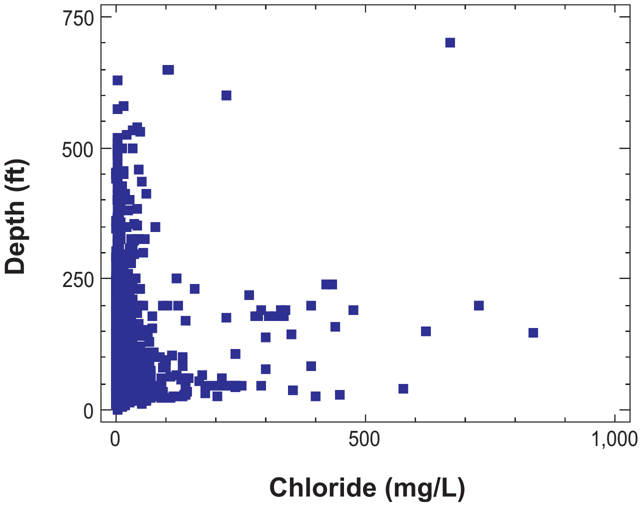

Figure 37. Chloride concentrations versus well depth. Values greater than 1,000 mg/L have been excluded to better show the majority of the results.

**Sulfate.** Sulfate ($SO_4$) is one of the major anions in most groundwater. The most significant sources of sulfate in groundwater are oxidation of iron sulfide minerals in coal or shale and dissolution of the calcium-sulfate minerals gypsum or anhydrite in carbonate strata.

There is no primary drinking-water standard for sulfate. The EPA has set a secondary standard of 250 mg/L because water containing more than 250 mg/L sulfate has an unpleasant taste that makes it unsuitable for domestic use. Water having sulfate concentrations greater than about 500 mg/L is a mild laxative.

The data set for sulfate is similar to that for conductance and chloride. Many sites that are identified as water wells have reported depths as great as 4,096 ft, and many wells do not have a depth recorded. In this data summary we excluded sulfate results from depths greater than 730 ft because the deepest groundwater sample reported by the Division of Water was 730 ft. Deeper wells are not likely to be used as groundwater supplies.

Table 11 summarizes sulfate measurements from groundwaters in BMU 3. Although the maximum value is 3,840 mg/L, 75 percent of the results are 40 mg/L or less, and more than 95 percent of the values are less than 250 mg/L (Fig. 38).

**Table 11.** Summary of sulfate values (mg/L).

| | |
|---|---|
| Measurements | 9,814 |
| Maximum | 3,840 |
| 75th percentile | 40 |
| Median | 11 |
| 25th percentile | 5 |
| Minimum | 0 |
| Interquartile range | 5–40 |
| Sites | 2,103 |
| SMCL | 250 |
| Sites > 250 | 173 |

The distribution of sampled sites and sites where sulfate concentrations exceed 250 mg/L (Fig. 39) is similar to that for chloride (Fig. 33). Sites where chloride exceeds 250 mg/L are clustered in the southern part of the Upper Cumberland River watershed, the eastern part of the Lower Cumberland River watershed, and in the northern part of the Tennessee River watershed.

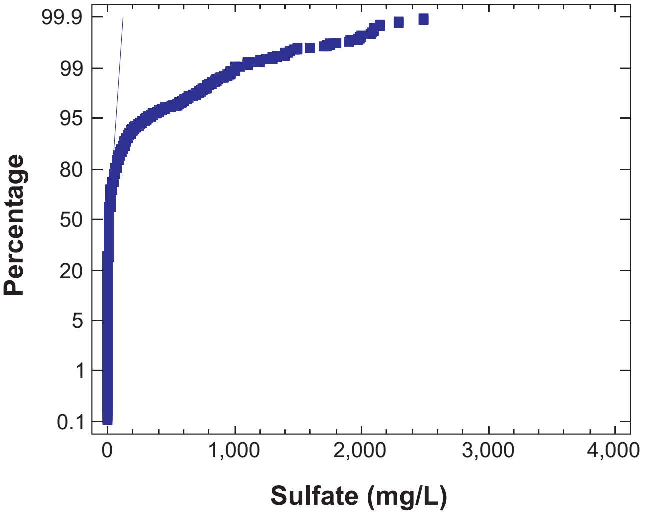

Figure 38. Cumulative plot of sulfate values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

All physiographic regions have produced groundwater with more than 1,000 mg/L sulfate (Fig. 40). No such values were found in the Mississippi River watershed in the Jackson Purchase Region, however (Fig. 41).

The highest sulfate concentrations are found in groundwater from wells, not springs (Fig. 42). This observation was also reported by Brown and Lambert (1963).

Although there is scatter in the data, sulfate concentrations generally increase from near surface to about 50 ft, then decrease with well depth (Fig. 43).

In summary, approximately 95 percent of the reported sulfate concentrations in BMU 3 are less than the SMCL of 250 mg/L. Natural oxidation of pyrite is the most probable cause of high sulfate concentrations in the Eastern Kentucky Coal Field, whereas dissolution of gypsum or anhydrite can yield high sulfate concentrations in the Eastern and Western Pennyroyal Regions. Dissolution of pyrite, gypsum, or anhydrite may produce high sulfate values in the Jackson Purchase Region.

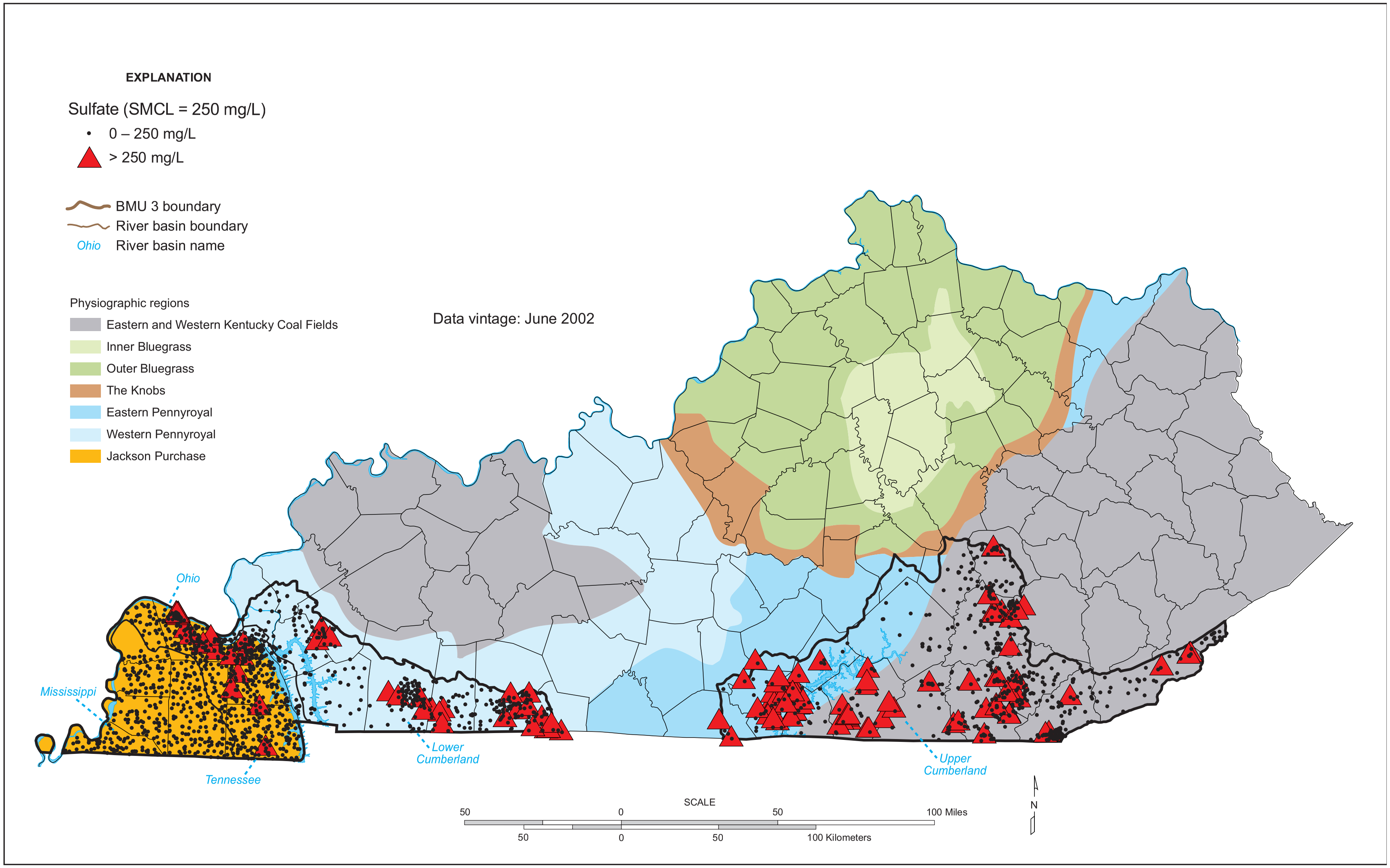

Figure 39. Sample sites and ranges of sulfate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

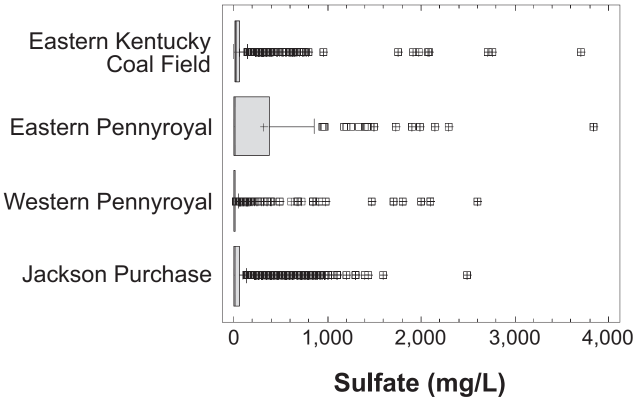

Figure 40. Summary of sulfate values grouped by physiographic region.

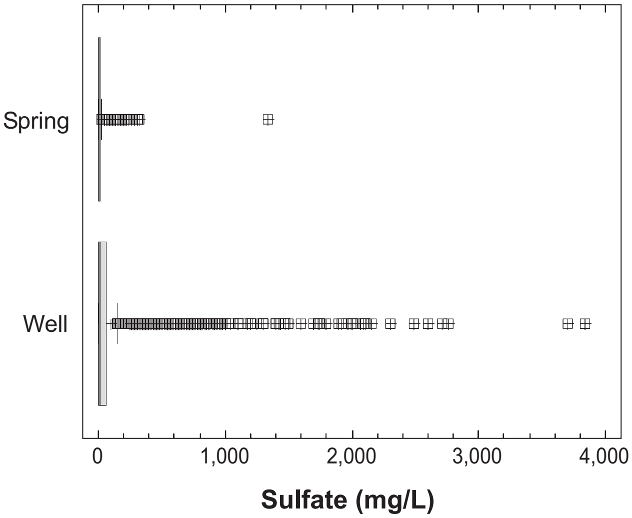

Figure 42. Comparison of sulfate values from wells and springs.

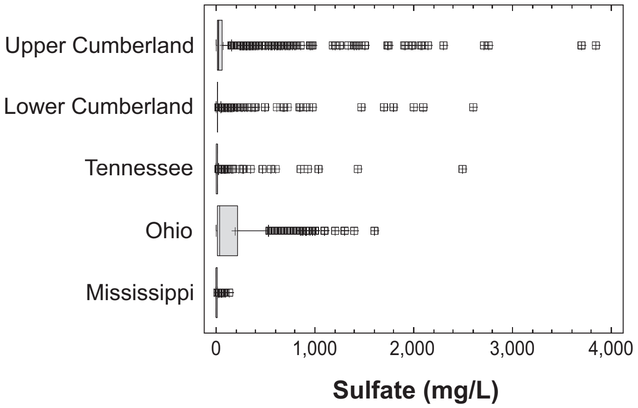

Figure 41. Summary of sulfate values grouped by major watershed.

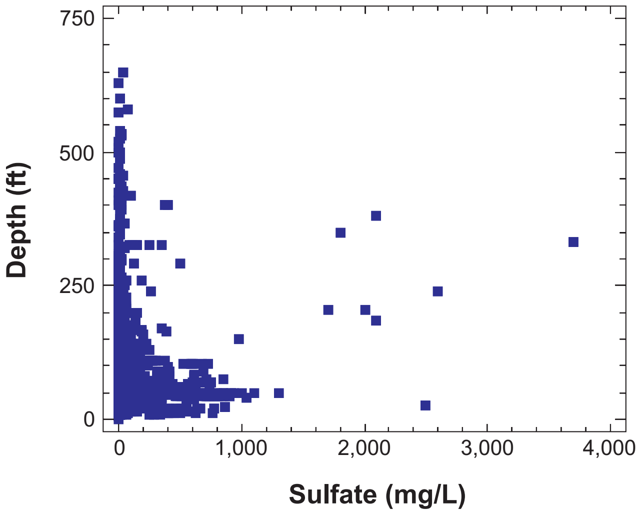

Figure 43. Sulfate values versus well depth.

**Fluoride.** Fluoride (F) is a minor anion, usually present in concentrations of less than 1 mg/L in groundwater. Natural sources of fluoride include the mineral fluorite ($CaF_2$), which is common in carbonate rocks. The major man-made sources are discharges from fertilizer and aluminum production facilities.

Fluoride is added to public water supplies in Kentucky to maintain a concentration of approximately 1 mg/L, because of its proven value in promoting healthy teeth and bones. At higher concentrations, fluoride may cause pain and weakness of the bones, and staining or mottling of teeth. The Environmental Protection Agency has established an MCL of 4 mg/L for fluoride in public drinking water.

Fluoride has been measured in 5,069 samples from 2,585 sites in BMU 3 (Table 12). The maximum value reported (78 mg/L) may be an error, although this cannot be confirmed. The second highest value is 19 mg/L. More than 99 percent of all measurements are less than 4.0 mg/L (Fig. 44).

**Table 12.** Summary of fluoride values (mg/L).

| | |
|---|---|
| Measurements | 5,069 |
| Maximum | 78 |
| 75th percentile | 0.20 |
| Median | 0.10 |
| 25th percentile | 0.10 |
| Minimum | 0.00 |
| Interquartile range | 0.10–0.20 |
| Sites | 2,585 |
| MCL | 4.0 |
| Sites > 4.0 | 26 |

Fluoride has been measured at many wells and springs throughout BMU 3 (Fig. 45). Concentrations greater than 4 mg/L are found mainly in the Upper Cumberland and Lower Cumberland River watersheds, and are rare in the Tennessee and Mississippi River watersheds (Fig. 45).

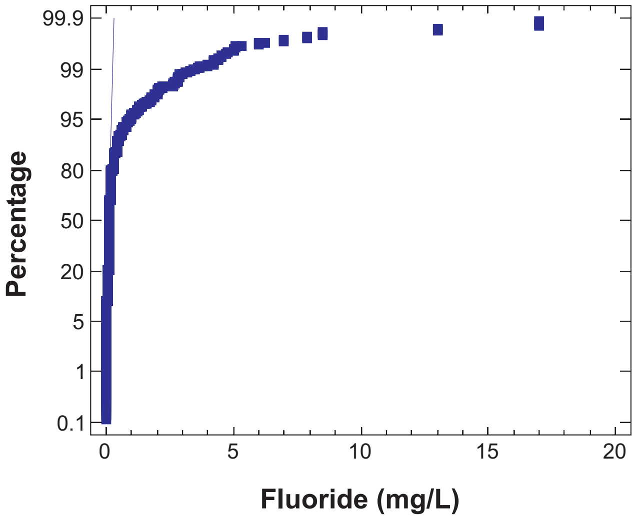

Figure 44. Cumulative plot of fluoride values. One value of 78 mg/L has been omitted so that the remaining data can be viewed more clearly.

Fluoride concentrations greater than 5 mg/L are found in the Eastern Kentucky Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland River watershed and the Western Pennyroyal Region of the Lower Cumberland River watershed (Figs. 46–47).

More fluoride concentrations greater than 4 mg/L are reported in groundwater from wells than from springs (Fig. 48). The majority of the fluoride data show a general increase with well depth to about 100 ft, followed by a decrease with further depth (Fig. 49).

In summary, the fluoride concentration of ambient groundwater samples in Basin Management Unit 3 is primarily controlled by bedrock lithology. Less than 1 percent of all reported analyses exceeded the EPA MCL of 4.0 mg/L. There are no obvious non-point-source contributions of fluoride to groundwater in the project area. A statewide summary of fluoride data (Conrad and others, 1999b) is available and can be viewed on the Kentucky Geological Survey Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

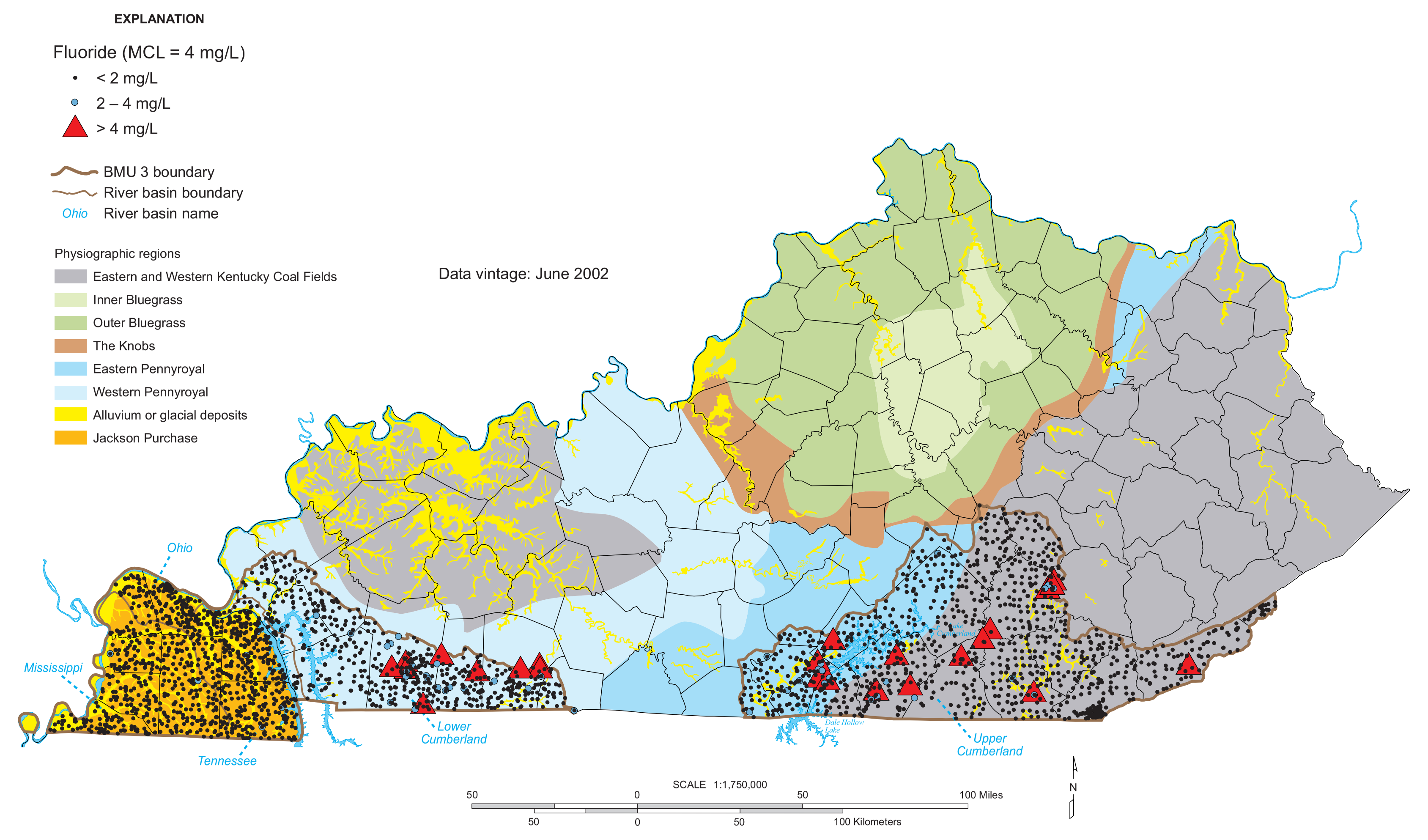

Figure 45. Sample sites and ranges of fluoride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

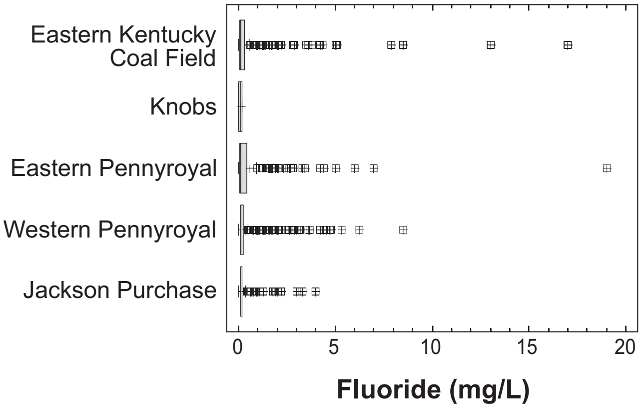

Figure 46. Summary of fluoride values grouped by physiographic region. One extreme value of 78 mg/L at a site in the Upper Cumberland watershed is probably erroneous and was omitted so that the majority of the data could be shown more clearly.

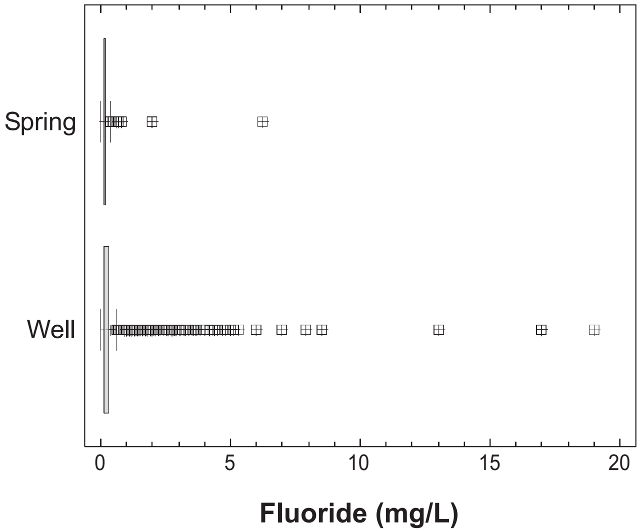

Figure 48. Comparison of fluoride values from wells and springs. One extreme value of 78 mg/L from a 62-ft-deep well is probably erroneous and was omitted so that the majority of the data could be shown more clearly.

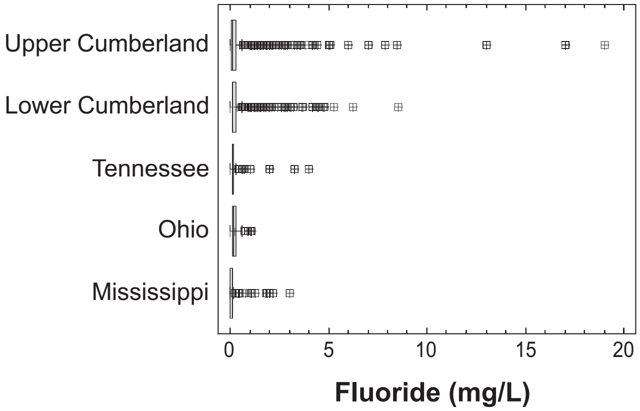

Figure 47. Summary of fluoride values grouped by major watershed. One extreme value of 78 mg/L at a site in the Eastern Kentucky Coal Field is probably erroneous and was omitted so that the majority of the data could be shown more clearly.

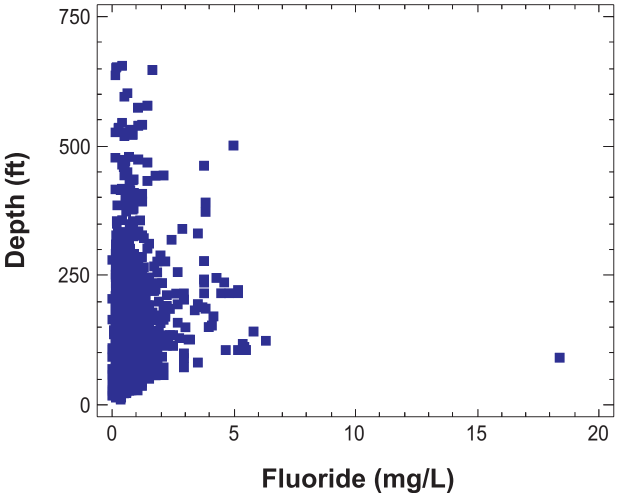

Figure 49. Fluoride values versus well depth. One extreme value of 78 mg/L from a 62-ft-deep well is probably erroneous and was omitted so that the majority of the data could be shown more clearly.

## *Metals*

**Arsenic.** Arsenic (As) is a naturally occurring element found in low concentrations in rocks, soils, water, plants, and animals (Nriagu, 1994a, b). In Kentucky, arsenic is commonly found in iron sulfide minerals associated with coal deposits and black shales. Arsenic is released when iron sulfides oxidize during weathering. Once released, arsenic is readily sorbed onto iron oxides and iron oxyhydroxides. This sorption can limit dissolved arsenic concentrations in groundwater, but can produce high arsenic concentrations in unfiltered groundwater samples that contain suspended particulate material (total arsenic concentrations).

Arsenic is used as a wood preservative and in paints, dyes, metals, drugs, soaps, semiconductors, animal feed additives, and herbicides. From 1860 through 1910 arsenic was heavily used in embalming fluids. It was banned in 1910 because it interfered with investigations into suspected poisoning deaths; old graveyards may still be a source of arsenic in groundwater (Fetter, 1993). Waste-disposal sites and landfills may be sources of arsenic contamination because of the materials disposed of there, and coal combustion can release arsenic to the atmosphere. Hydrocarbons from leaking underground storage tanks can dissolve iron oxide minerals in soils, thus releasing naturally occurring arsenic to the environment (Welch and others, 2000). Metal-reducing bacteria, as well as changes in oxidation conditions as a result of pumping, also can affect arsenic concentrations in the vicinity of a well.

Long-term exposure to arsenic in drinking water has been linked to health problems such as cancer of the skin, bladder, lungs, kidneys, nasal passages, liver, and prostate. Arsenic has also been linked to damage of the cardiovascular, pulmonary, immunological, neurological, and endocrine systems (U.S. Environmental Protection Agency, 1998). The EPA set the MCL for arsenic in drinking water at 0.050 mg/L in 1974. In 2001 the EPA announced that this MCL will be lowered to 0.010 mg/L. Water-supply systems must meet the new MCL beginning in January 2006.

Both total and dissolved arsenic analyses were performed with a variety of methods and detection limits. Approximately 70 percent of the records are reported as less than a detection limit, with detection limits ranging from 0.052 to 0.001 mg/L. Because the new MCL is 0.010 mg/L, measurements reported only as below a detection limit, in which the detection limit was 0.010 or greater, provide no useful information. Therefore, these values are not included in the following discussion. Removing those values leaves a total of 1,477 measured arsenic concentrations at 308 sites (Table 13). Sixty-six percent of the values were reported as less than a detection limit. Forty-five of 308 sites have total arsenic concentrations greater than 0.010 mg/L, but only seven sites have dissolved arsenic concentrations greater than 0.010 mg/L. More than 90 percent of reported values are less than 0.010 mg/L (Fig. 50).

**Table 13.** Summary of arsenic values (mg/L).

| | |
|---|---|
| Measurements | 1,086 |
| Maximum | 0.219 |
| 75th percentile | < 0.002 |
| Median | < 0.002 |
| 25th percentile | < 0.002 |
| Minimum | 0.001 |
| Interquartile range | na |
| Sites | 188 |
| MCL | 0.010 |
| Sites > 0.010 | 28 |

< means analytical result reported as less than the stated value

Sites where arsenic was measured are fairly evenly distributed throughout the project area, with clusters of sites in the northern Tennessee and Ohio River watersheds (Fig. 51).

Arsenic concentrations exceed 0.010 mg/L in all physiographic regions except the Western Pennyroyal (Fig. 52) and all major watersheds except the Lower Cumberland (Fig. 53).

Total arsenic concentrations range to higher values than dissolved arsenic concentrations, although there is considerable overlap of the values (Fig. 54). Dissolved arsenic concentrations measure a filtered sample; total arsenic concentrations measure an unfiltered sample. Well purging can stir up sediment, and arsenic that is adsorbed onto the sediment would be analyzed as part of the total sample. Arsenic associated with suspended solids would be less mobile than

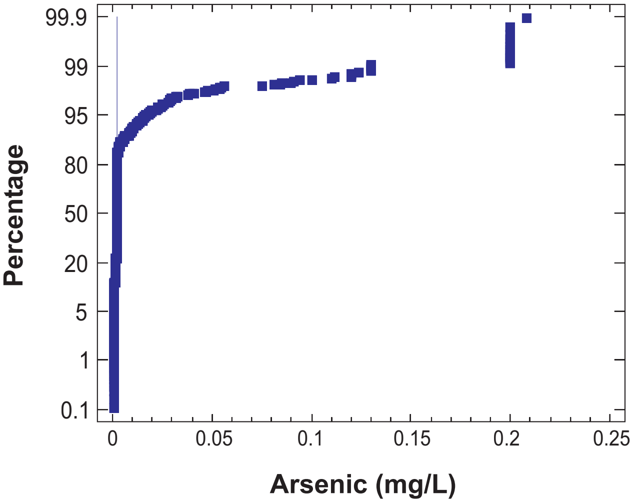

Figure 50. Cumulative plot of arsenic values. Higher values were excluded to show values in the range of the MCL.

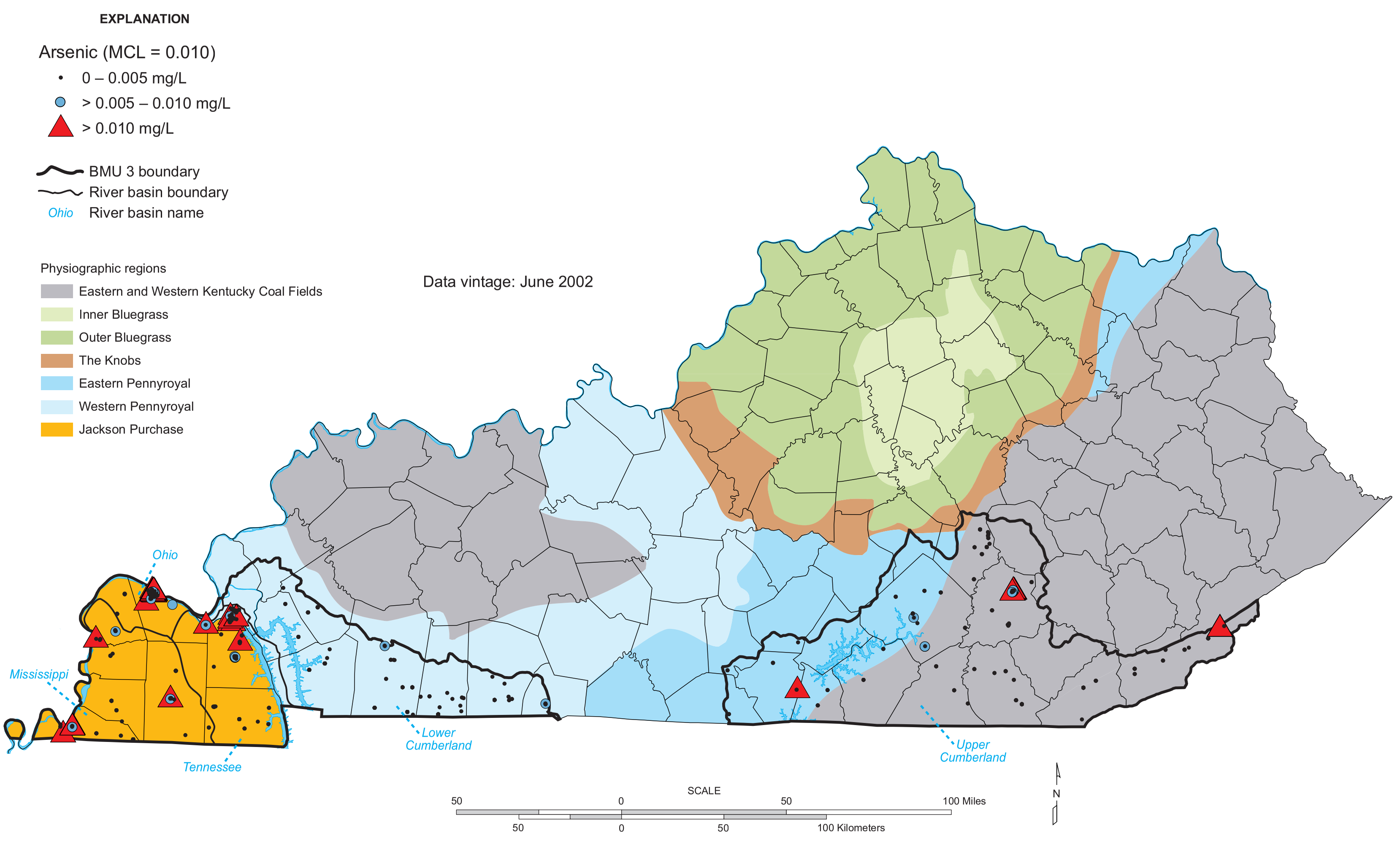

Figure 51. Sample sites and ranges of arsenic values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

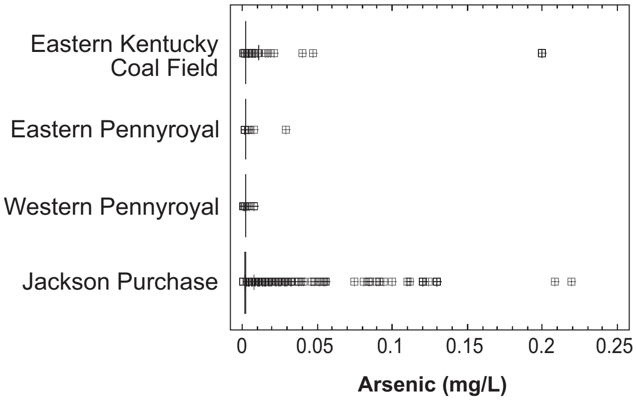

Figure 52. Summary of arsenic values grouped by physiographic region.

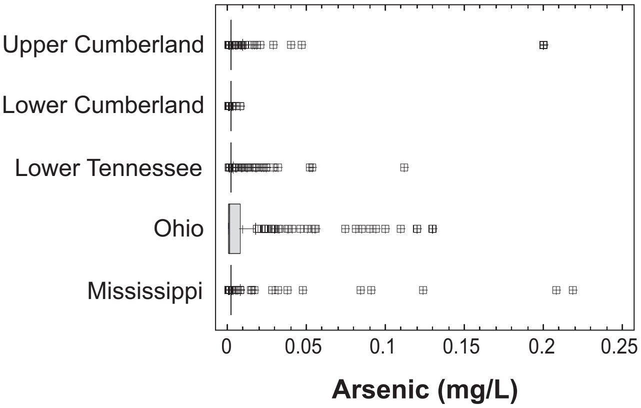

Figure 53. Summary of arsenic values grouped by major watershed.

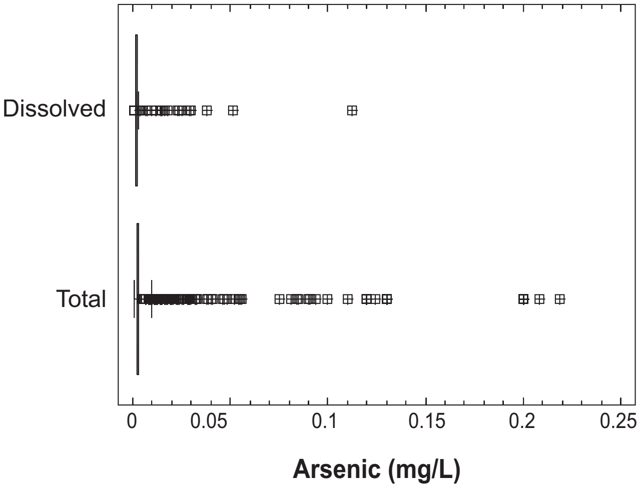

Figure 54. Comparison of total and dissolved arsenic values.

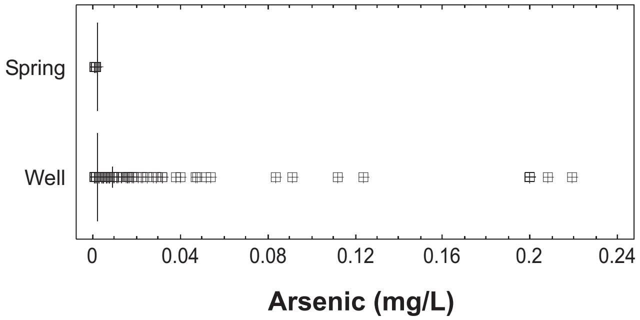

Figure 55. Comparison of arsenic values from wells and springs.

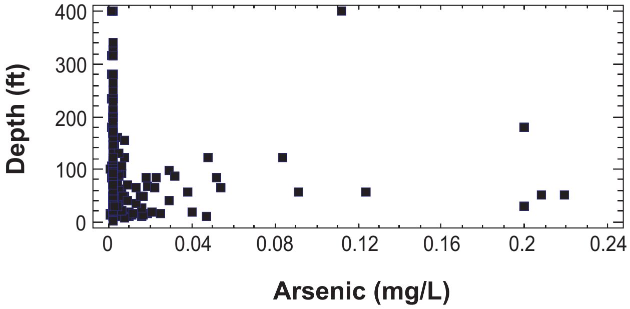

Figure 56. Arsenic concentrations versus well depth.

arsenic in true solution in the groundwater. Therefore, if an individual site showed a high total arsenic concentration but low dissolved arsenic concentration, the arsenic is probably not mobile in a porous-media groundwater system. Dissolved arsenic (or other metals) is probably in true aqueous solution and therefore mobile in the groundwater system, however.

Samples from wells have more instances of high arsenic values than samples from springs (Fig. 55), and relatively shallow wells (30 to 80 ft deep) generally have the highest arsenic concentrations (Fig. 56).

In summary, most wells and springs in the project area produce water with arsenic levels well below the 0.010 mg/L MCL. Sites where arsenic concentrations exceed the MCL are most common in the Jackson Purchase Region. Arsenic concentrations are generally higher in unfiltered water samples than in filtered samples, suggesting an association between arsenic and suspended particulate material. High arsenic concentrations are more likely to be found in wells than in springs, and more likely to be found in the shallow groundwater system (wells less than 100 ft deep) than in deeper flow systems. Local changes in oxidation/reduction state caused by pumping or metal-reducing bacteria may lead to higher arsenic concentrations near a wellbore than in the regional groundwater system. A statewide summary of arsenic data (Fisher, 2002a) is available and can be viewed on the Kentucky Geological Survey Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

**Barium.** Barium (Ba) is an alkaline earth element that occurs naturally as the mineral barite ($BaSO_4$). Barite is a common mineral in both sandstone and carbonate strata. Barium is used in electronic components, metal alloys, bleaches, dyes, fireworks, ceramics, and glass, and as an additive to drilling fluids used in oil and gas wells. Barium may be released to soil and water from the discharge of drilling wastes, or from leaking landfills where barium-containing materials were discarded.

The MCL for barium is 2 mg/L. Short-term exposure to higher barium concentrations can cause gastrointestinal problems and muscular weakness, whereas long-term exposure can cause high blood pressure.

Barium concentrations in groundwater from BMU 3 are generally well below levels of concern. The data repository contained 1,712 barium measurements from 389 sites, with no values greater than the MCL of 2.0 mg/L (Table 14). More than 99 percent of the measurements are less than 0.5 mg/L (Fig. 57).

**Table 14.** Summary of barium values (mg/L).

| | |
|---|---|
| Measurements | 1,712 |
| Maximum | 1.200 |
| 75th percentile | 0.057 |
| Median | 0.038 |
| 25th percentile | 0.019 |
| Minimum | < 0.0007 |
| Interquartile range | 0.019–0.057 |
| Sites | 389 |
| MCL | 2.0 |
| Sites > 2.0 | 0 |

< means analytical result reported as less than the stated value

Sites are uniformly distributed throughout the project area, except for a large cluster in the northern Tennessee River watershed and a smaller cluster in the Ohio River watershed (Fig. 58). Barium concentrations greater than 1.0 mg/L are found in the Eastern Kentucky Coal Field of the Upper Cumberland River watershed and the Jackson Purchase Region (Ohio, Tennessee, and Mississippi River watersheds) (Figs. 58–60).

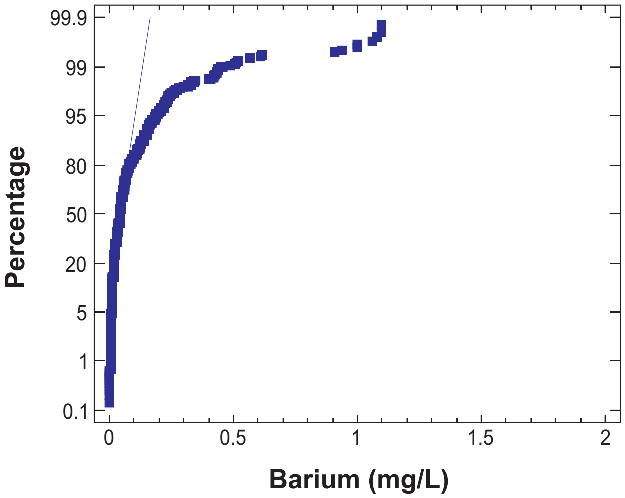

Figure 57. Cumulative plot of barium values in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Barium concentrations greater than 0.5 mg/L are found only in unfiltered samples (total barium), not in filtered samples (dissolved barium), indicating that barium is associated with suspended particulate material (Fig. 61). Similarly, barium concentrations greater than 0.5 mg/L are found only in samples from wells, not from springs (Fig. 62). Higher barium concentrations are reported from wells less than 100 ft deep than from deeper wells that sample slower groundwater flow systems (Fig. 63).

Wells between approximately 50 and 100 ft deep have higher barium concentrations than deeper wells (Fig. 63).

In summary, barium concentrations in BMU 3 groundwater are generally well below the health-based MCL established by the EPA. Barium concentrations do not appear to be affected by nonpoint-source factors, but are more likely the result of natural hydrogeologic processes. The highest barium concentrations are found in unfiltered groundwater samples from wells that are between 50 and 100 ft deep.

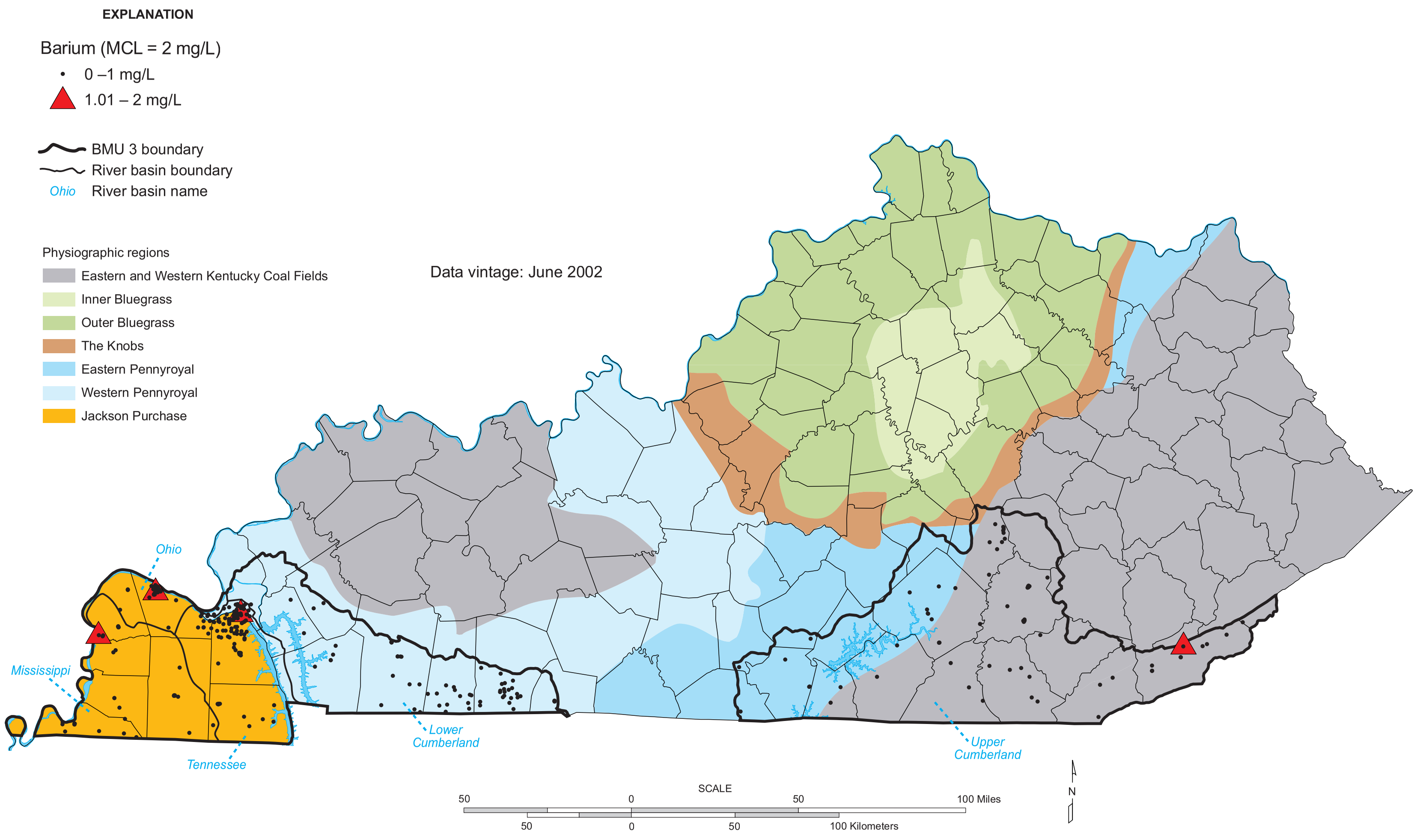

Figure 58. Sample sites and ranges of barium values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

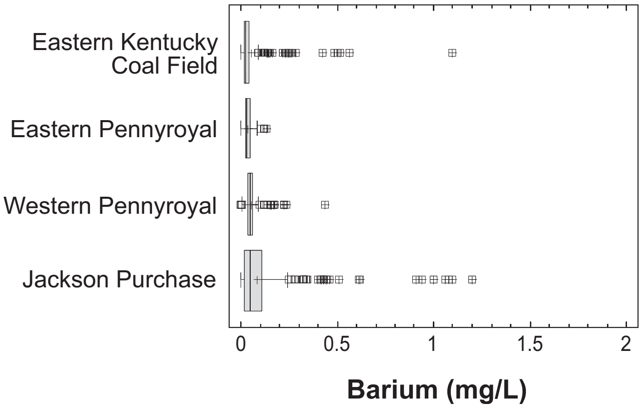

Figure 59. Summary of barium values grouped by physiographic region.

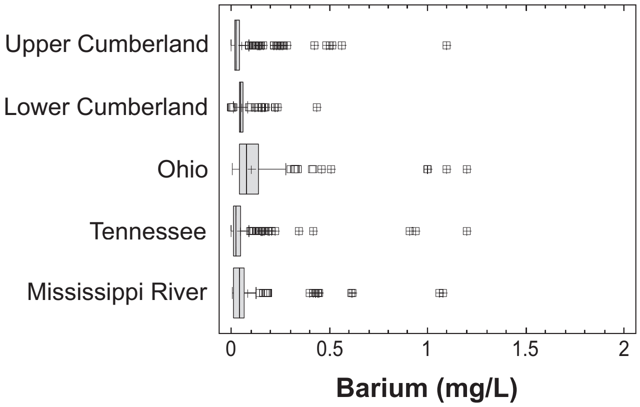

Figure 60. Summary of barium values grouped by major watershed.

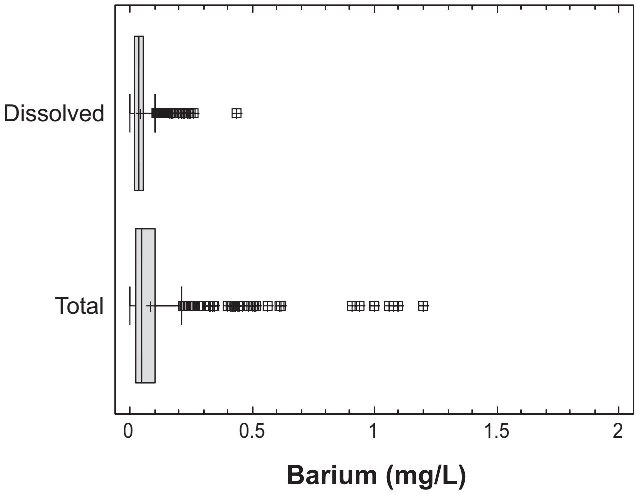

Figure 61. Comparison of total and dissolved barium values. Values greater than 1.5 mg/L were omitted to better show the majority of reported analytical results.

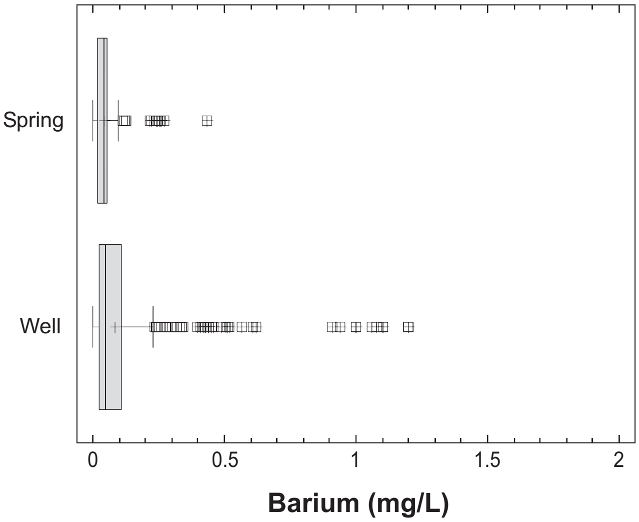

Figure 62. Comparison of barium values from wells and springs.

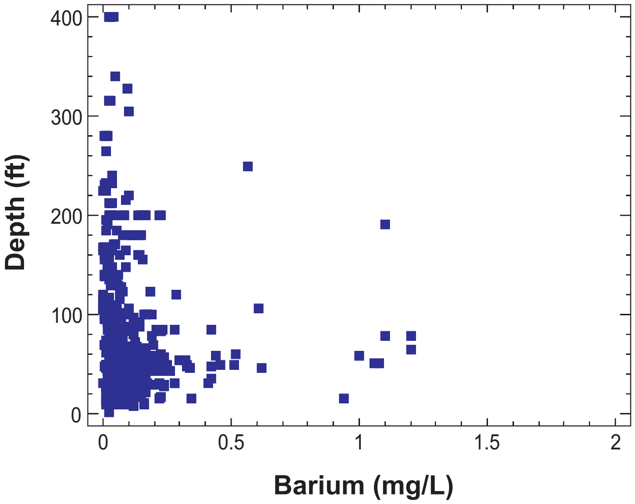

Figure 63. Barium values versus well depth.

**Iron.** Iron (Fe) is a naturally occurring metal that is widely present in groundwater. Iron can occur in either an oxidized (ferric) or reduced (ferrous) state. At normal groundwater pH values, ferric iron is rapidly precipitated as an iron oxide, iron hydroxide, iron oxyhydroxides (rust), or as poorly crystalline to amorphous material. Under reduced conditions, however, ferrous iron is stable and will remain dissolved in groundwater. There is no EPA primary drinking-water standard for iron in water supplies. There is a secondary standard of 0.3 mg/L, however, because higher iron concentrations will produce objectionable odor, taste, color, staining, corrosion, and scaling.

The data repository contained 8,809 iron measurements from 2,148 sites (Table 15). Values range from 1,040 to 0.0 mg/L, with a median value of 0.34 mg/L. Iron concentrations were greater than 0.3 mg/L at 1,213 sites in BMU 3.

**Table 15.** Summary of iron values (mg/L).

| | |
|---|---|
| Measurements | 8,809 |
| Maximum | 1,040 |
| 75th percentile | 1.81 |
| Median | 0.34 |
| 25th percentile | 0.08 |
| Minimum | 0.00 |
| Interquartile range | 0.08–1.81 |
| Sites | 2,148 |
| SMCL | 0.3 |
| Sites > 0.3 | 1,213 |

Approximately 95 percent of the measured values are less than 10 mg/L; however, there are many higher values (Fig. 64).

Sample sites are densely distributed throughout the project area, particularly in the eastern part of the Eastern Kentucky Coal Field and the Jackson Purchase Region (Fig. 65). Sites where iron exceeds 0.3 mg/L are common throughout BMU 3.

The Western Pennyroyal Region (Fig. 66) and the Lower Cumberland River watershed (Fig. 67) are the only areas in BMU 3 where all iron concentrations are less than 100 mg/L.

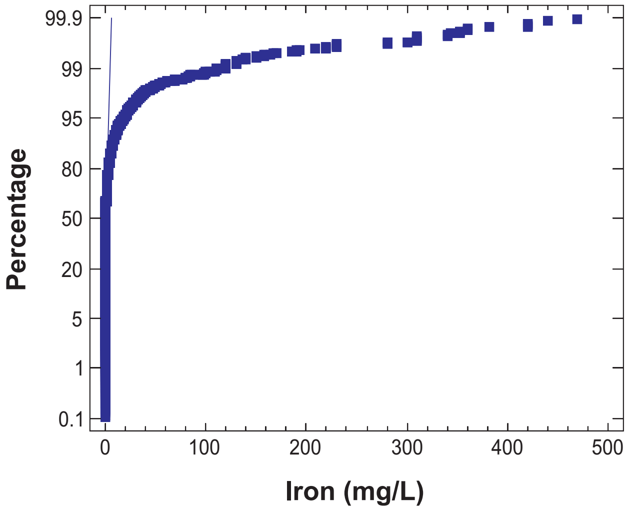

Figure 64. Cumulative plot of iron values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

The highest reported iron concentrations are from unfiltered samples (total iron) (Fig. 68) and from samples collected from wells rather than from springs (Fig. 69).

The highest iron concentrations are found in wells shallower than about 200 ft (Fig. 70).

In summary, approximately half the wells and springs in the project area produce groundwater with less than 0.3 mg/L iron. Many wells and springs produce water with much higher iron concentrations, however. Total iron concentrations are typically higher than dissolved iron concentrations, indicating that suspended particulate material also contributes iron to the analysis. Wells produce groundwater with higher iron concentrations than springs. This reflects the expected trend of oxidation conditions. Water in springs is generally more highly oxidized, and therefore iron would precipitate out, whereas water from wells is more likely to be reduced, and therefore iron will remain in solution. Groundwater users should test each well or spring before using the water for domestic purposes to avoid the problems of taste and staining associated with high iron in groundwater. There is no evidence that nonpoint-source contamination significantly contributes to iron concentrations in the project area.

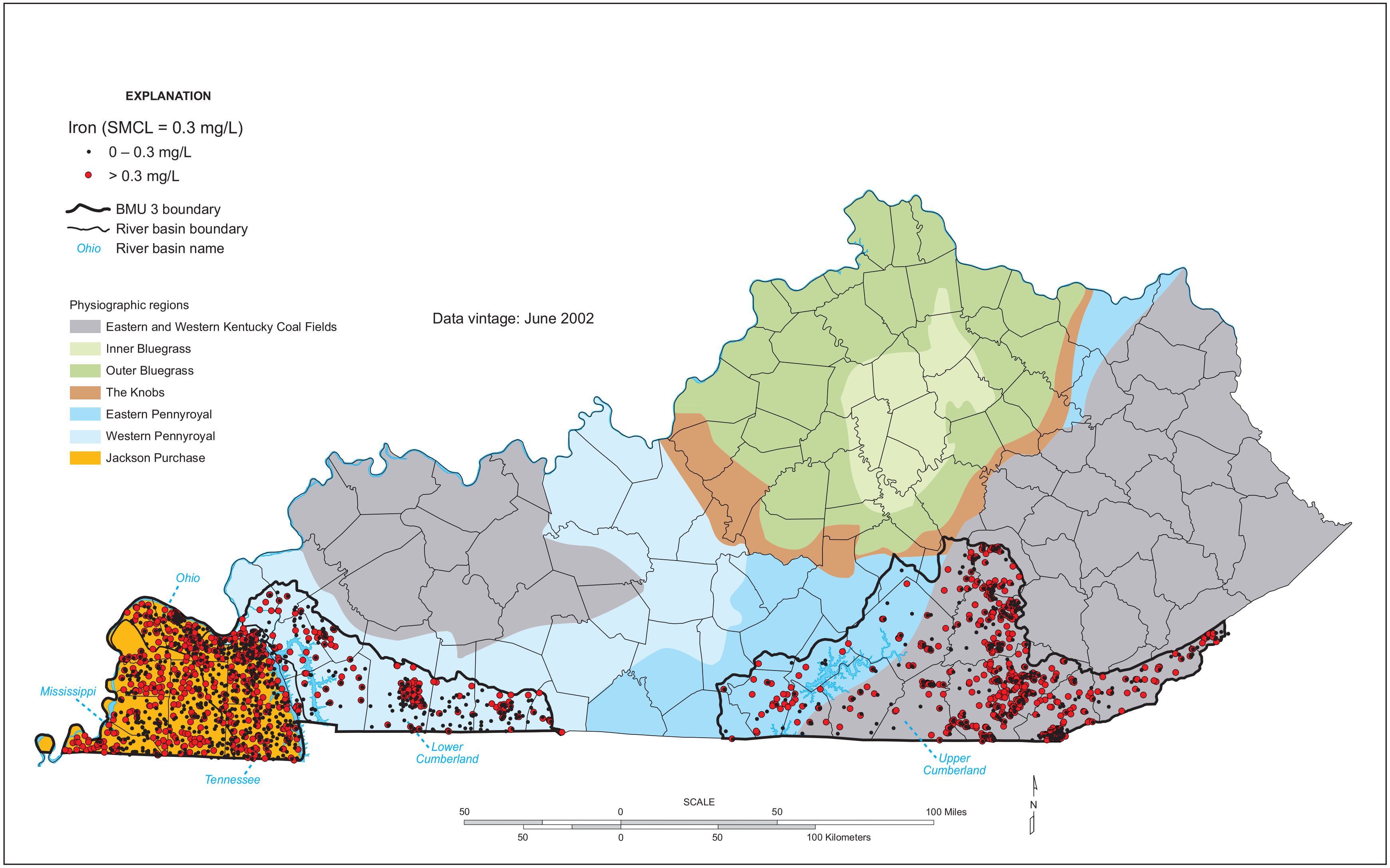

Figure 65. Sample sites and ranges of iron concentrations.

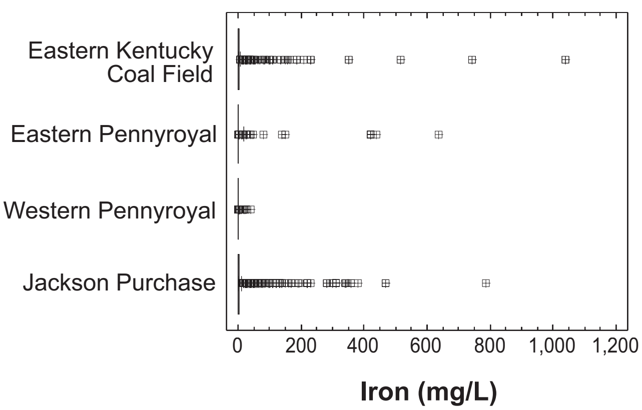

Figure 66. Comparison of iron values grouped by physiographic region. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

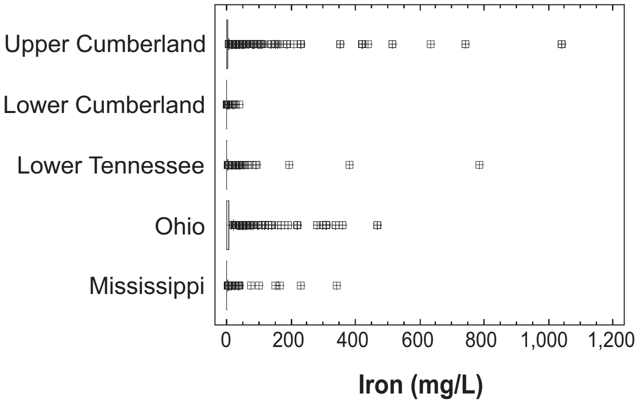

Figure 67. Comparison of iron values grouped by major watershed. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

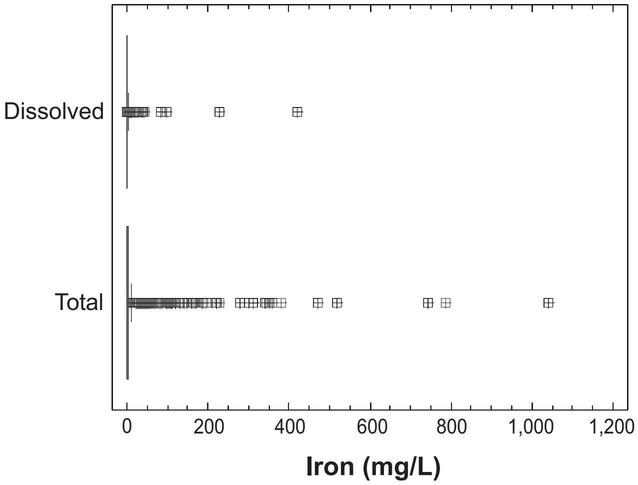

Figure 68. Comparison of total and dissolved iron values. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

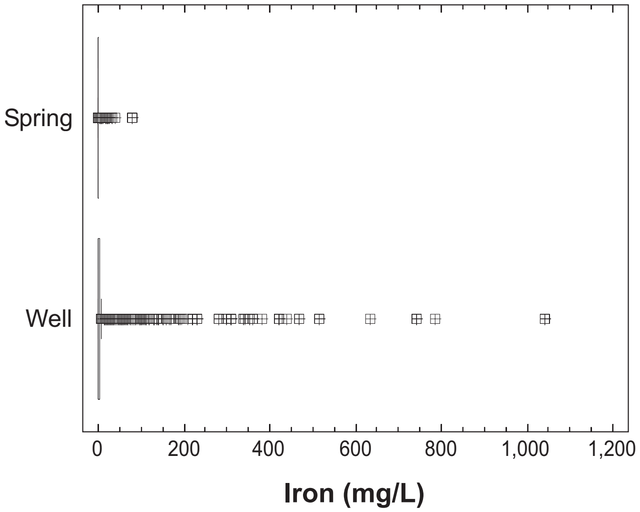

Figure 69. Comparison of iron values from wells and springs. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

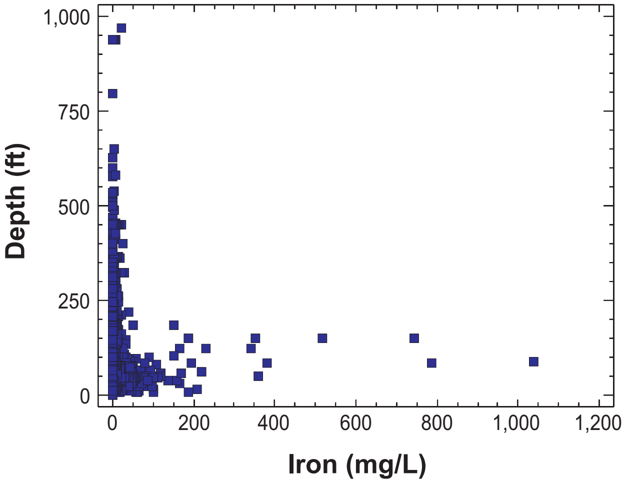

Figure 70. Iron values versus well depth. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

**Manganese.** Manganese (Mn) is a naturally occurring cation that is widely present in groundwater supplies. Geochemically, manganese and iron behave similarly, so high manganese concentrations can be expected from wells and springs that produce water with high iron concentrations.

There is no MCL for manganese in water supplies. The secondary standard is 0.05 mg/L; higher concentrations produce objectionable odor, taste, color, corrosion, and staining.

The data repository contained 6,469 manganese measurements at 2,013 sites. Values range from 0.0 to 114 mg/L (Table 16). Manganese concentrations exceeded 0.05 mg/L at approximately 56 percent of the sites (Table 16). Approximately 40 percent of reported manganese concentrations are less than 0.05 mg/L and approximately 80 percent are less than 1.0 mg/L (Fig. 71).

**Table 16.** Summary of manganese values (mg/L).

| | |
|---|---|
| Measurements | 6,469 |
| Maximum | 114 |
| 75th percentile | 0.32 |
| Median | 0.076 |
| 25th percentile | 0.011 |
| Minimum | 0.00 |
| Interquartile range | 0.011–9,329 |
| Sites | 2,013 |
| SMCL | 0.05 |
| Sites > 0.05 | 1,138 |

Distribution of sample sites in BMU 3 is dense (Fig. 72). More sites where manganese exceeds 0.05 mg/L are located in the Eastern Kentucky Coal Field and northern part of the Eastern Pennyroyal than in the other physiographic regions (Fig. 72).

The highest reported manganese values are from sites in the Eastern Kentucky Coal Field and Western Pennyroyal (Fig. 73). Only two analyses were reported from The Knobs Region. Figure 74 compares manganese values by major watershed.

The highest reported manganese concentrations are total analyses (unfiltered sample) (Fig. 75).

Groundwater with the highest manganese concentrations comes from wells rather than from springs (Fig. 76).

Shallow wells yield the highest reported manganese concentrations (Fig. 77). With two exceptions, manganese concentrations are near zero in samples from wells deeper than 200 ft.

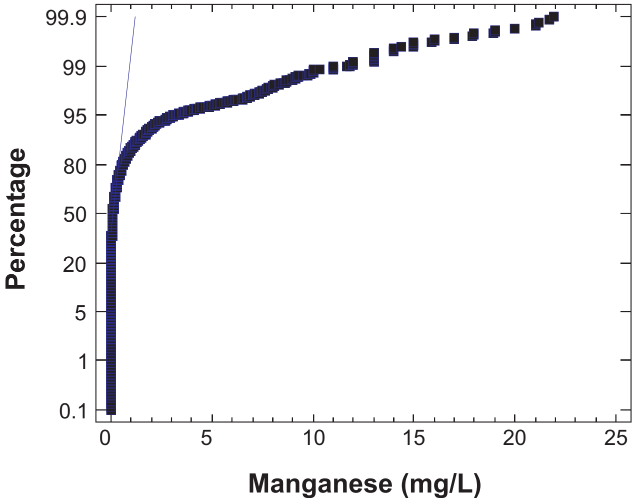

Figure 71. Cumulative plot of manganese values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

In summary, manganese concentrations above the SMCL occur in all major watersheds, and all physiographic regions. Manganese and iron are geochemically similar and behave similarly in the environment. Comparison of the map showing sites where manganese exceeds 0.05 mg/L (Fig. 72) with the map of high iron concentrations (Fig. 65) shows the similar pattern. Like iron, manganese is readily sorbed onto suspended material and is less soluble under oxidizing conditions than in reducing environments. This geochemical property is illustrated by the observation that total (unfiltered sample) manganese concentrations are higher than dissolved (filtered sample) concentrations (Fig. 75), and that high manganese concentrations are less common in groundwater from springs than in well water (Fig. 76). Very high manganese concentrations (greater than 5 mg/L) are much more common in shallow wells than in groundwater from deeper wells. The geochemical similarity between manganese and iron is demonstrated in the similarity of their concentrations in groundwater. Both commonly occur at concentrations that affect groundwater taste and can produce staining of containers and clothing. There is no evidence to suggest that nonpoint-source contamination significantly contributes to manganese concentrations in the project area.

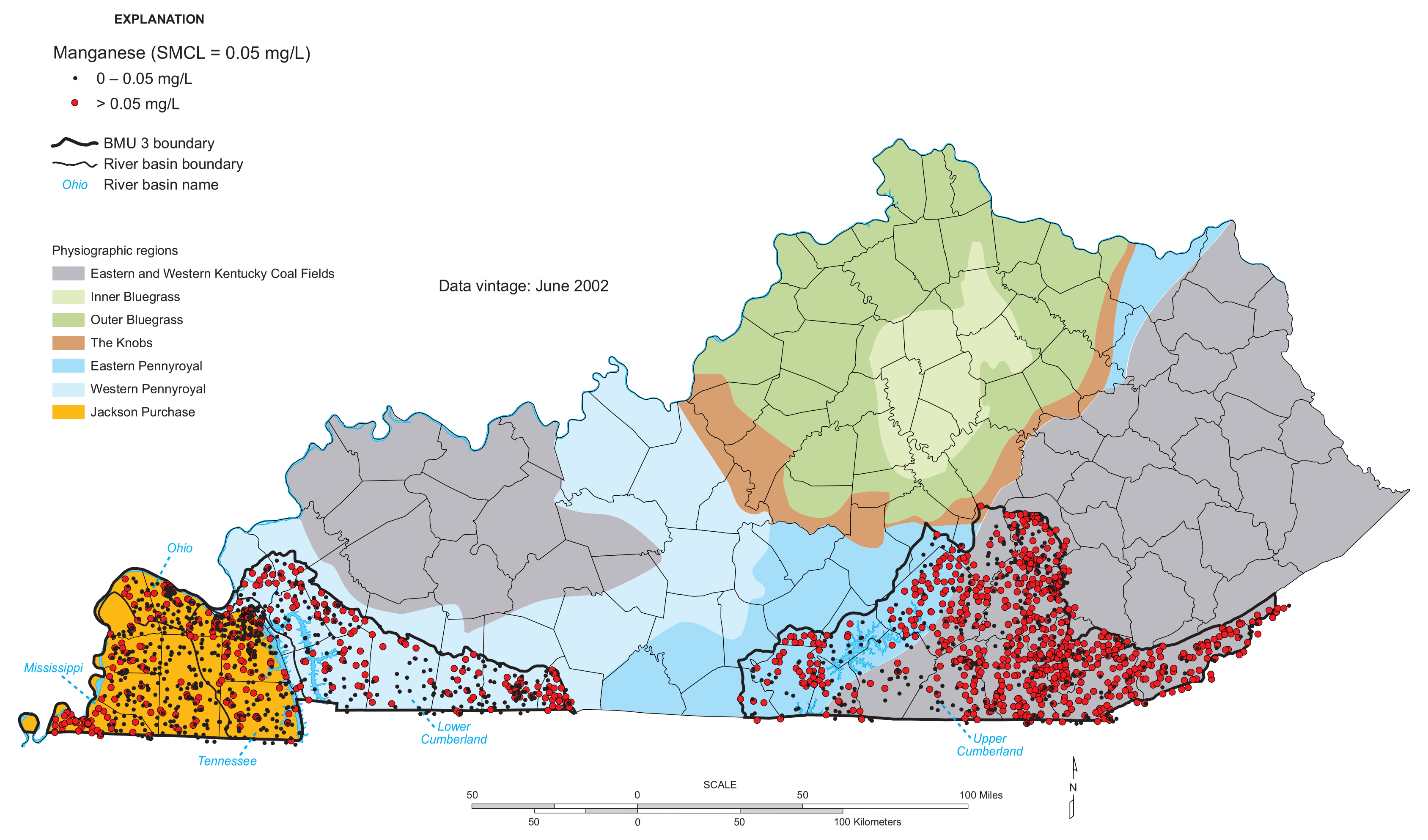

Figure 72. Sample sites and ranges of manganese concentrations.

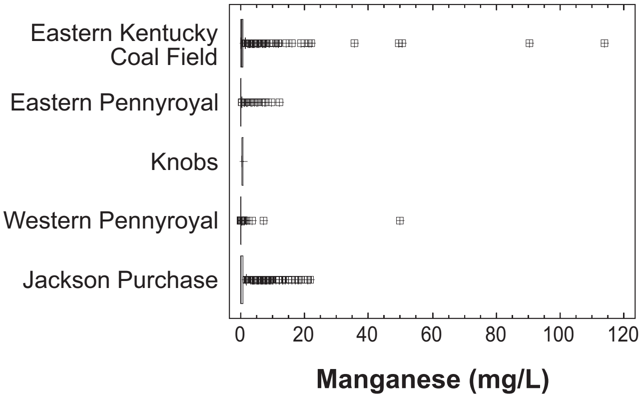

Figure 73. Comparison of manganese values grouped by physiographic region.

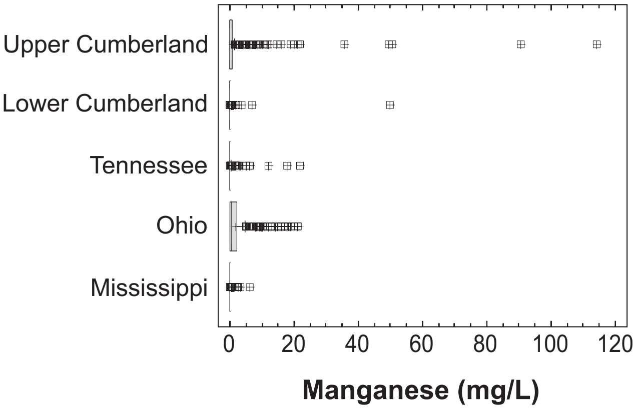

Figure 74. Comparison of manganese values grouped by major watershed.

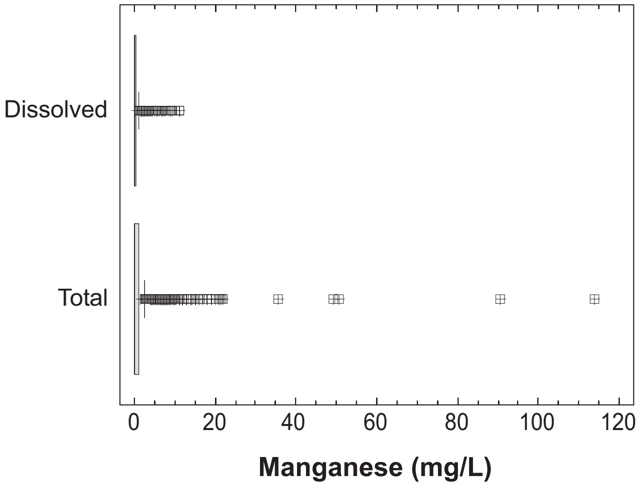

Figure 75. Comparison of total and dissolved manganese values.

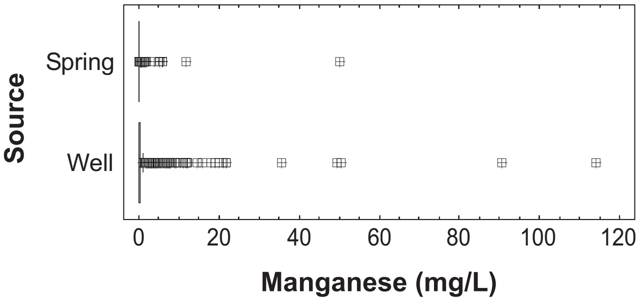

Figure 76. Summary of manganese concentrations grouped by site type.

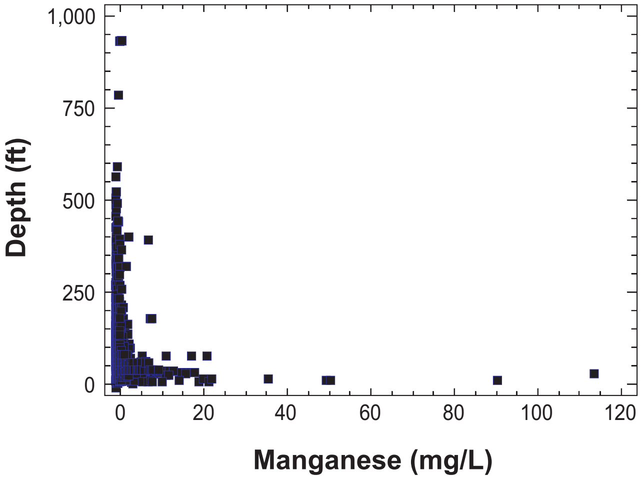

Figure 77. Manganese values versus well depth.

**Mercury.** Mercury (Hg) is a liquid metal found in natural deposits that also contain other elements. Forest fires, coal combustion products, disposal of mercury-containing products such as electric lights and switches, computers, thermometers, and blood-pressure gages contribute mercury to the environment. Electrical products such as dry-cell batteries, fluorescent light bulbs, switches, and other control equipment account for 50 percent of mercury used. Combustion of fossil fuels, metal smelters, cement manufacture, municipal landfills, sewage, and metal refining operations are significant sources of mercury in the environment. When mercury from such sources is acted on by bacteria, some of it is converted to methyl mercury, a much more toxic form of mercury.

Because of its toxicity, the EPA has set an MCL value for mercury at 0.002 mg/L. At high doses mercury is a strong neurotoxin that causes demyelination[2], delayed nerve conduction, and kidney damage.

The groundwater data repository contained 1,001 mercury analyses from 269 sites from the project area (Table 17). Approximately 87 percent of the analyses were reported as less than an analytical detection limit. Only four sites yielded groundwater with mercury concentrations greater than 0.002 mg/L. The median value was less than a detection limit of 0.00005 mg/L (Table 17). More than 95 percent of the reported values are less than 0.002 mg/L (Fig. 78).

**Table 17.** Summary of mercury values (mg/L).

| | |
|---|---|
| Measurements | 1,001 |
| Maximum | 0.01750 |
| 75th percentile | < 0.00005 |
| Median | < 0.00005 |
| 25th percentile | < 0.00005 |
| Minimum | < 0.00005 |
| Interquartile range | na |
| Sites | 269 |
| MCL | 0.002 |
| Sites > 0.002 | 4 |

< means analytical result reported as less than the stated value

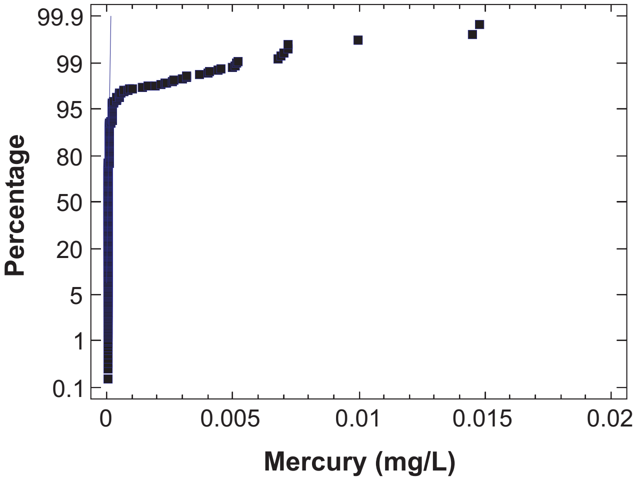

Figure 78. Cumulative plot of mercury values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Sites where mercury was measured are uniformly distributed throughout the project area, with one cluster of sites in the northern Tennessee River watershed (Fig. 79). Mercury concentrations exceed the MCL in the Tennessee River watershed of the Jackson Purchase Region (Figs. 79–81).

The highest mercury concentrations are found in unfiltered samples (total mercury) rather than filtered samples (dissolved mercury) (Fig. 82). No dissolved mercury concentrations greater than 0.001 mg/L were reported.

Wells produce groundwater with higher mercury concentrations than springs (Fig. 83). Shallow wells produce higher mercury concentrations than intermediate or deep wells (Fig. 84).

In summary, mercury is rarely present in detectable amounts in groundwater from wells or springs in the project area. There is no evidence of nonpoint-source impacts on mercury concentrations in Kentucky groundwater in the project area. Mercury concentrations greater than 0.001 mg/L occur only in total samples and probably represent mercury associated with suspended sediment rather than in true solution.

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[2] Destruction or loss of material that acts as a sheath around nerves.

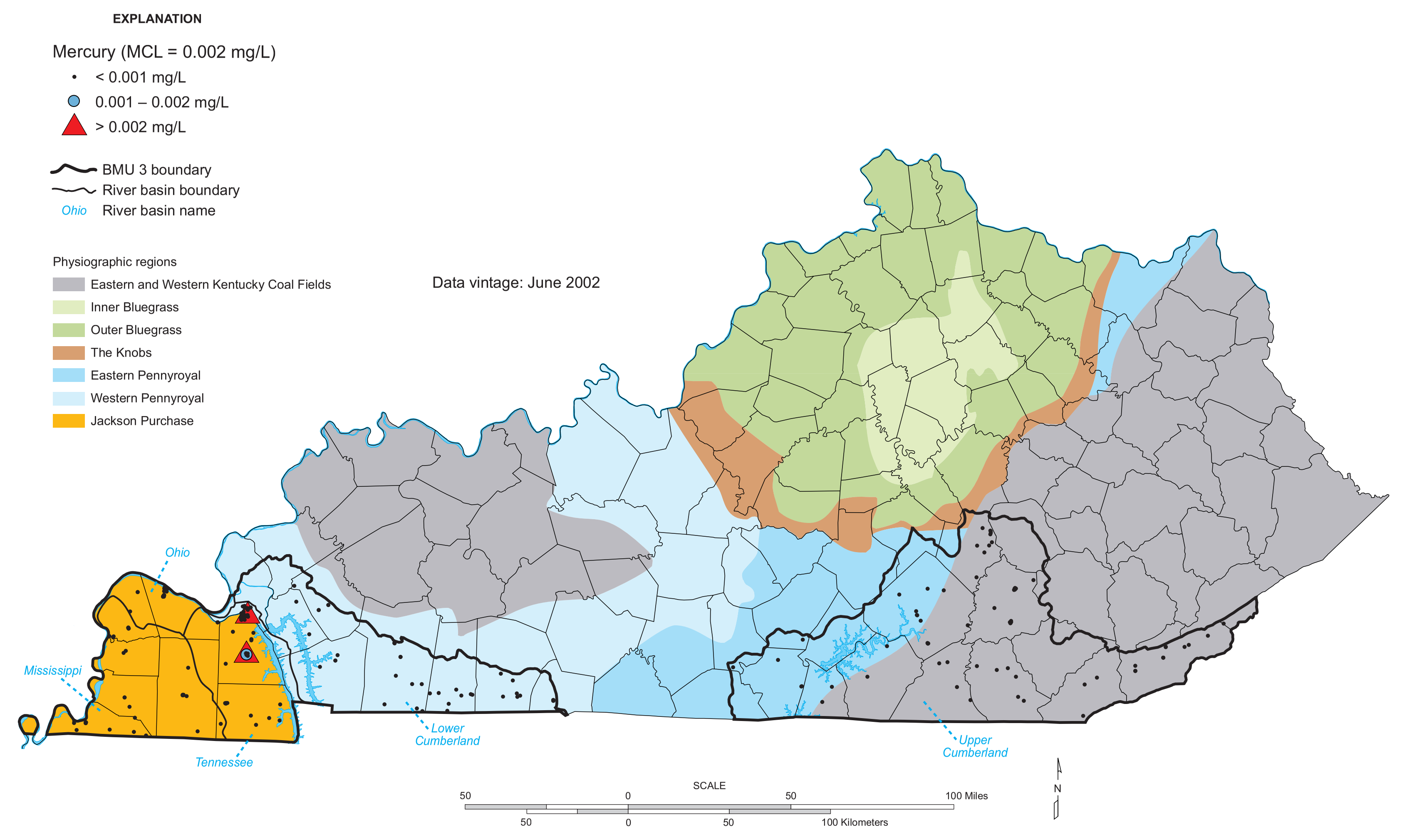

Figure 79. Sample sites and ranges of mercury values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

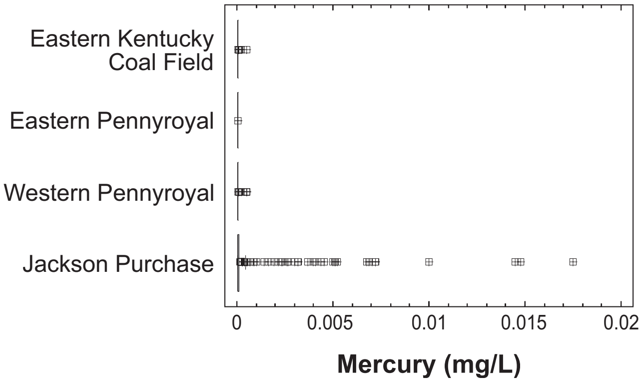

Figure 80. Comparison of mercury values grouped by physiographic region.

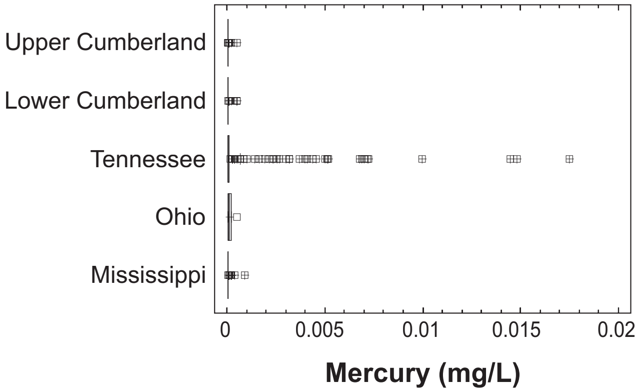

Figure 81. Comparison of mercury values grouped by major watershed.

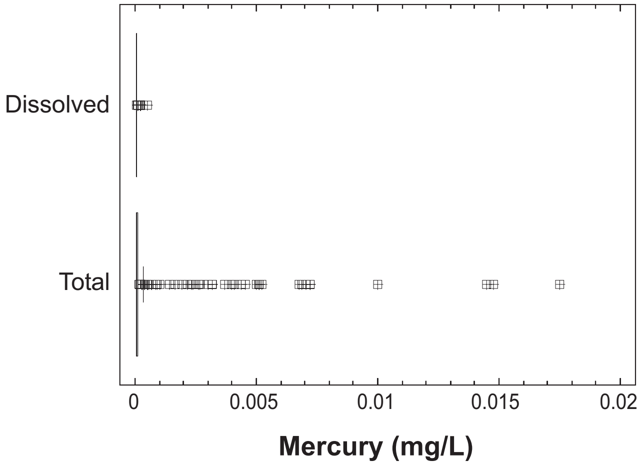

Figure 82. Comparison of dissolved and total mercury values.

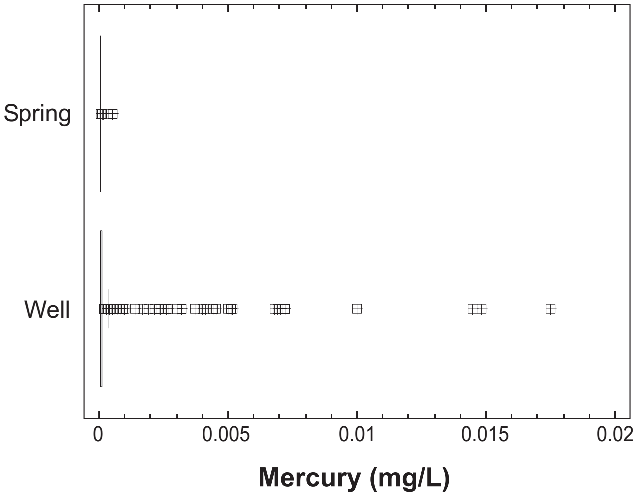

Figure 83. Comparison of mercury values in springs and wells.

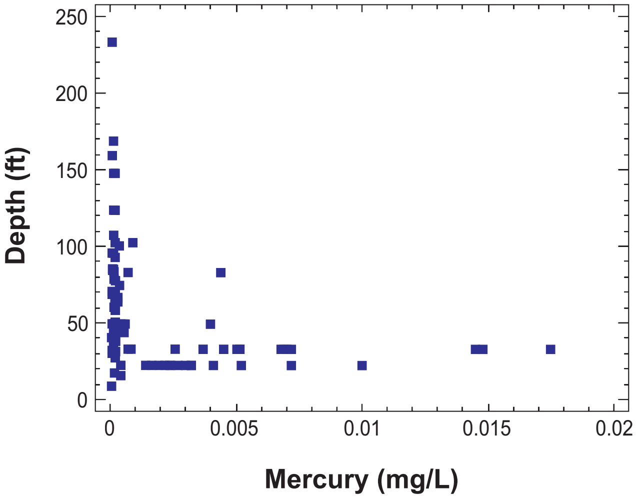

Figure 84. Mercury concentrations versus well depth. Only concentrations reported as above detection limits are shown.

## Nutrients

The nutrients nitrogen and phosphorus occur naturally and also may be introduced to groundwater systems from urban and agricultural fertilizer applications, livestock or human wastes, and fossil-fuel combustion. High nutrient levels in groundwater generally indicate contamination from fertilizer, sewage systems, or confined feedlot operations. Excessive nutrients can lead to algal blooms and eutrophication in surface-water systems, and excessive nitrate or nitrite in drinking water can pose health hazards.

**Nitrogen Species.** Nitrogen in water occurs predominantly as either the anion nitrate ($NO_3^-$) under oxidizing conditions or the cation ammonium ($NH_4^+$) under reducing conditions. Nitrite ($NO_2^-$) and ammonia ($NH_3$) are thermodynamically less stable forms of aqueous nitrogen that may be present under reducing conditions. Because it is positively charged, ammonium is readily adsorbed on soil and mineral particles, thus limiting its mobility, whereas the negatively charged nitrate and nitrite anions are highly mobile. Nitrite, ammonium, and ammonia are unstable in oxidizing environments such as aerated groundwater (Hem, 1985). For this reason, high concentrations of these species in shallow groundwater are indicators of likely contamination by sewage or other forms of organic waste. These reduced forms of nitrogen may also occur in a deep, reducing groundwater system.

Runoff from fertilizer use, leachate from septic tanks, and sewage are major sources of nitrogen species. Nitrate is commonly used in fertilizer. High nitrate concentrations generally indicate contamination by fertilizer or by either human or animal organic waste. Caves in karst terrain that are home to large bat colonies may accumulate large amounts of guano that contribute nitrogen to local groundwater. Nitrite concentrations in groundwater are generally low because nitrite reacts quickly to nitrate in oxidizing environments and to nitrogen gas in reducing environments (Fetter, 1993).

Nitrate, nitrite, ammonia, and ammonium concentrations are reported differently for different purposes. Analyses for geochemical investigations traditionally report concentrations as weight per volume of the measured ions (mg/L of $NO_3^-$, $NO_2^-$, $NH_3$, or $NH_4^+$). Analyses for environmental purposes, however, generally report the concentrations as equivalent amounts of nitrogen (nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, or ammonium-nitrogen). Consequently, nitrogen data must be examined closely to determine how they were recorded, and concentration units must be standardized before data summaries and evaluations can be made.

The EPA has established a drinking-water MCL of 10 mg/L for nitrate-nitrogen (equivalent to 44.3 mg/L as nitrate) and 1.0 mg/L for nitrite-nitrogen (equivalent to 3.2 mg/L as nitrite). Higher concentrations can lead to methemoglobinemia (blue baby syndrome) in infants, in which the oxygen-carrying ability of the child's blood is severely reduced. Lifetime exposure to nitrite-nitrogen concentrations greater than 1 mg/L also can produce diuresis, increased starchy deposits and hemorrhaging of the spleen. No human health-based concentration limits have been established for ammonia or ammonium. Ammonia concentrations of 1 to 10 mg/L can be toxic to aquatic life, however.

*Nitrate-Nitrogen.* The data repository contained 7,085 nitrate-nitrogen measurements from 1,518 sites (Table 18). The maximum value (99 mg/L) far exceeds the MCL of 10 mg/L. The third quartile and median values are below the MCL of 10 mg/L. About 6 percent of the sites in BMU 3 yielded water with nitrate-nitrogen greater than 10 mg/L.

**Table 18.** Summary of nitrate-nitrogen values (mg/L of N).

| | |
|---|---|
| Measurements | 7,085 |
| Maximum | 99 |
| 75th percentile | 5.31 |
| Median | 4.38 |
| 25th percentile | 1.11 |
| Minimum | 0.00 |
| Interquartile range | 1.11–6.31 |
| Sites | 1,518 |
| MCL | 10.0 |
| Sites > 10.0 | 90 |

The data distribution for measurements from BMU 3 (Fig. 85) has two inflection points, which suggests the presence of two different populations of values. This probably reflects the diverse physiographic regions and resulting land uses (mining, forestry, and agriculture) in BMU 3. More than 95 percent of the reported measurements are less than 10 mg/L.

Nitrate has been measured at many sites throughout BMU 3 (Fig. 86). The highly agricultural Jackson Purchase Region is the most densely sampled and contains the greatest number of sites where nitrate concentrations exceed 10 mg/L. The mostly agricultural Eastern and Western Pennyroyal Regions have also been well sampled and have many sites where nitrate concentrations exceed the MCL. Few sites in the Eastern Kentucky Coal Field exceed 10 mg/L.

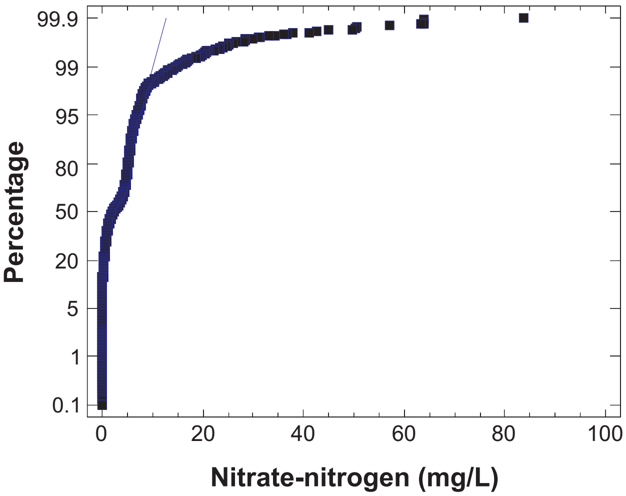

Figure 85. Cumulative plot of nitrate-nitrogen concentrations. Values greater than 90 mg/L have been omitted to show detail in the lower concentration ranges.

Grouping nitrate concentrations by physiographic region (Fig. 87) and major watershed (Fig. 88) shows that concentrations exceeding the MCL occur in all watersheds and regions. Although the Jackson Purchase Region has the greatest number of sites where nitrate-nitrogen exceeds 10 mg/L (Fig. 87) the highest reported nitrate concentrations are found in the Western Pennyroyal Region (Fig. 87), Lower Cumberland River watershed (Fig. 88). Furthermore, the middle 50 percent of reported values from the Western Pennyroyal Region, Lower Cumberland River watershed, are higher than the central 50 percent of values from any other region or watershed.

Water wells yielded the highest nitrate concentrations (Fig. 89). The central 50 percent of reported values are higher in water from springs than from wells, however. The highest nitrate concentrations are found in wells shallower than about 150 ft (Fig. 90).

In summary, approximately 6 percent of all sites produced groundwater with nitrate-nitrogen concentrations that exceed the MCL. Based on the distribution of such sites, it is highly likely these are in areas where agricultural chemicals are used, where there are animal holding facilities, or sewage is not properly disposed of. Nearly 54 percent of the sites have produced groundwater with more than 5.0 mg/L nitrate-nitrogen. Many, if not all, of these are probably affected by nonpoint-source sources of nitrate. Wells less than 150 ft deep are more likely to produce high-nitrate groundwater than deeper wells or springs.

A statewide summary of nitrate data (Conrad and others, 1999a) is available and can be viewed on the Kentucky Geological Survey Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

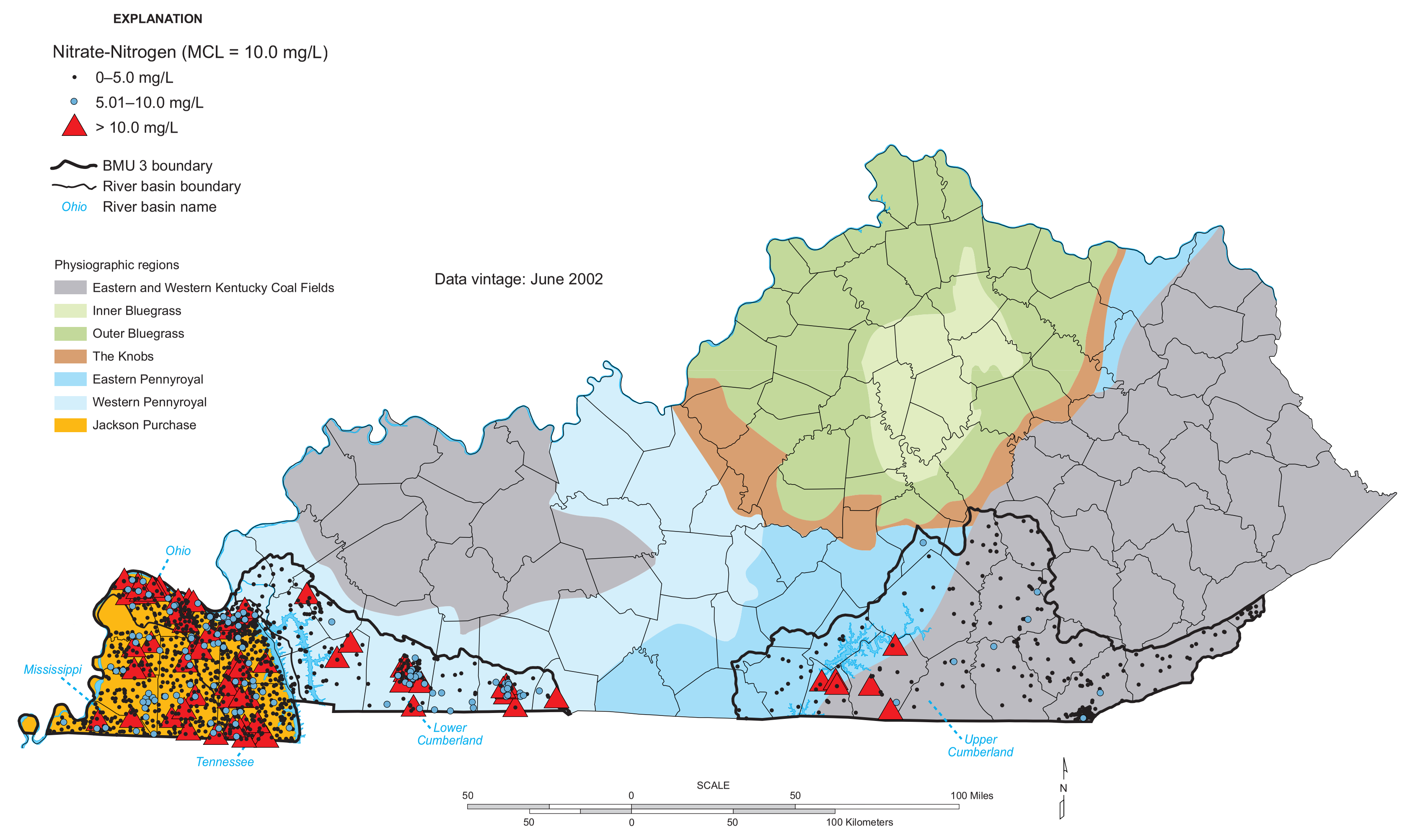

Figure 86. Sample sites and nitrate-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

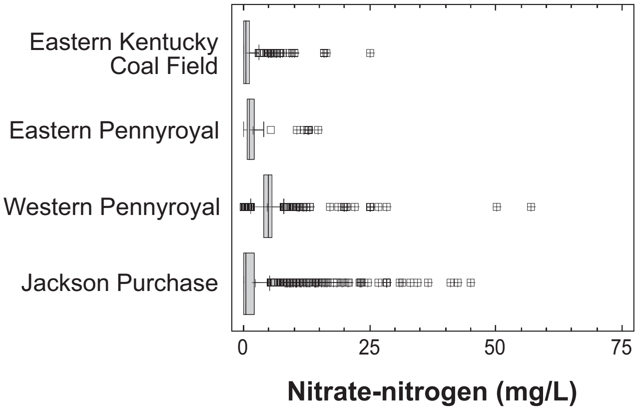

Figure 87. Summary of nitrate-nitrogen values grouped by major watershed. Values greater than 60 mg/L were omitted to show detail in the lower concentration ranges.

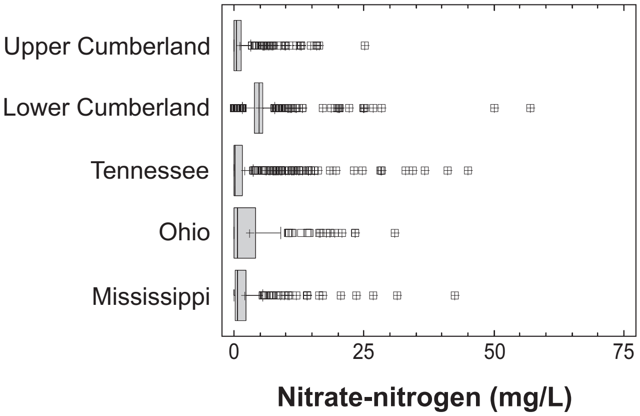

Figure 88. Summary of nitrate-nitrogen data grouped by physiographic region. Values greater than 60 mg/L were omitted to show detail in the lower concentration ranges.

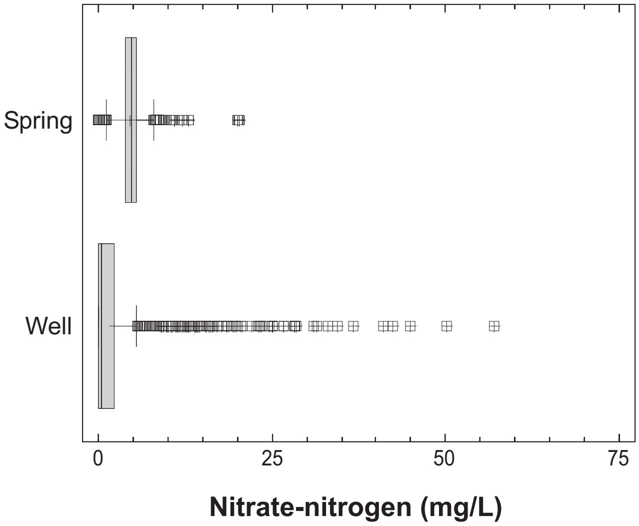

Figure 89. Comparison of nitrate-nitrogen concentrations from wells and springs. Values greater than 60 mg/L have been omitted to show detail in the lower concentration ranges.

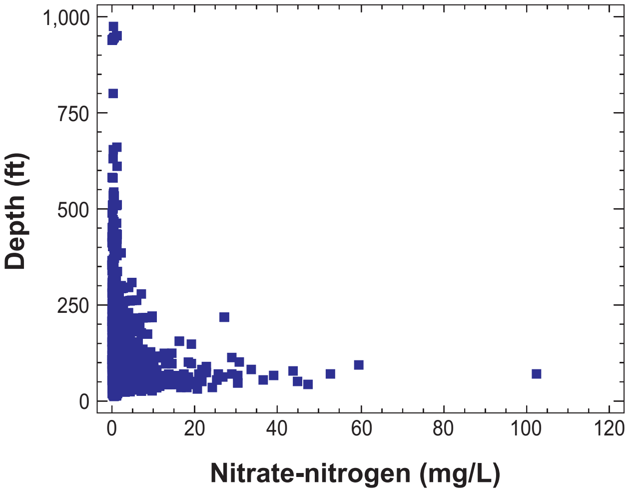

Figure 90. Nitrate concentrations versus well depth.

*Nitrite-Nitrogen.* The data repository contained 753 measurements of nitrite-nitrogen from 116 sites (Table 19). No reported concentrations exceeded the EPA health-based MCL of 1.0 mg/L, and only four values were greater than 0.10 mg/L.

Few sites have been sampled for nitrite-nitrogen (Fig. 91). Because of the sparse data and the absence of any reported concentration that exceeded the MCL, no further analyses were performed.

In summary, no sites in the project area produced groundwater with nitrite-nitrogen concentrations over the MCL. In light of the many high nitrate-nitrogen concentrations reported, the absence of high nitrite-nitrogen values is most likely the result of the thermodynamic instability of nitrite, rather than absence of nitrogen inputs.

**Table 19.** Summary of nitrite-nitrogen values (mg/L of N).

| | |
|---|---|
| Measurements | 753 |
| Maximum | 0.274 |
| 75th percentile | 0.009 |
| Median | 0.005 |
| 25th percentile | 0.002 |
| Minimum | 0.00 |
| Interquartile range | 0.002–0.009 |
| Sites | 116 |
| MCL | 1.0 |
| Sites > 1.0 | 0 |

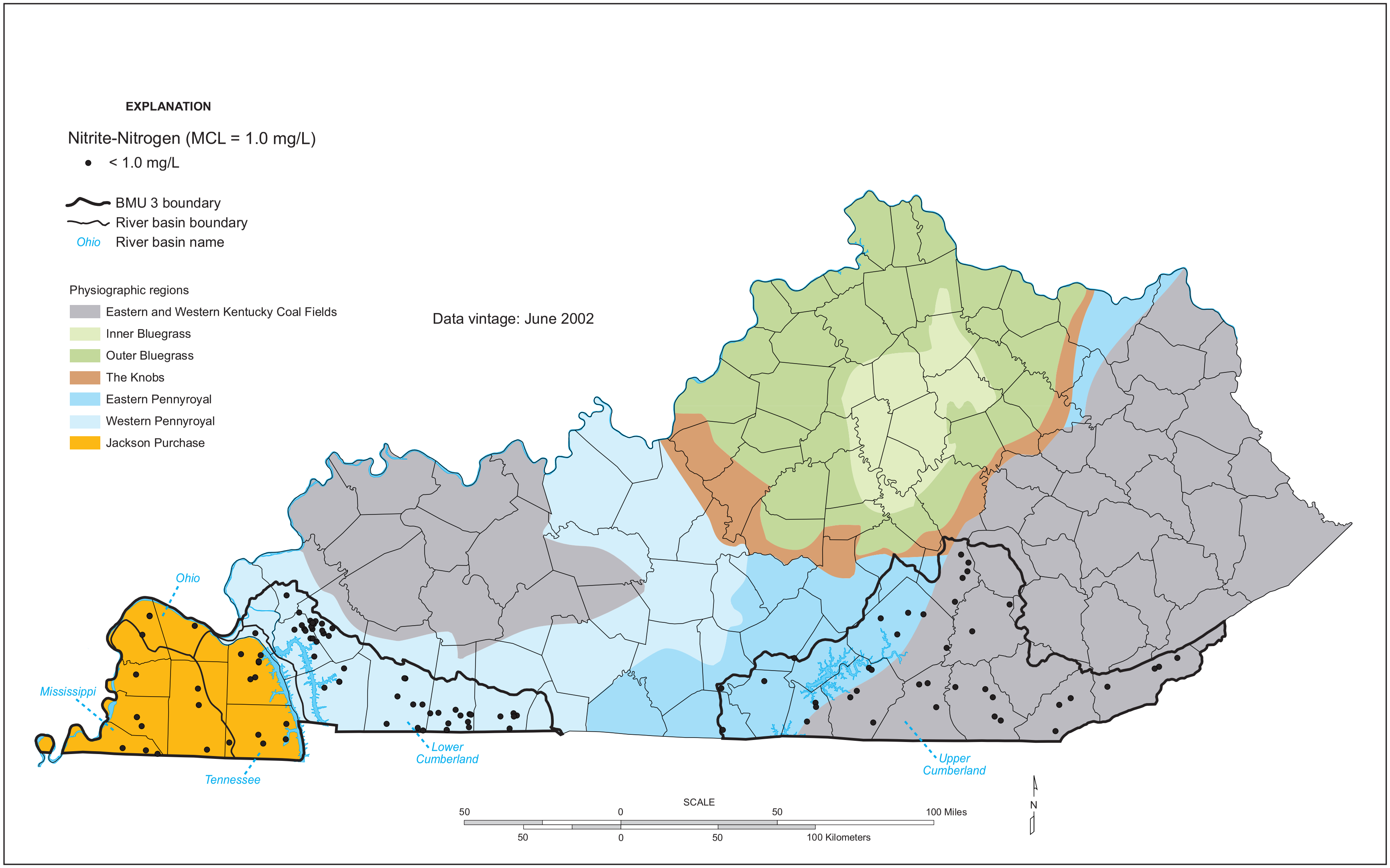

Figure 91. Sites where nitrite-nitrogen has been measured.

*Ammonia-Nitrogen.* The data repository contained 932 ammonia-nitrogen measurements from 146 sites in BMU 3 (Table 20). Although there are no EPA health-based standards for ammonia-nitrogen, the Kentucky Department for Environmental Protection has recommended a risk-based upper limit of 0.110 mg/L. Values exceeding 0.110 mg/L were observed at 17 sites in BMU 3. The highest value (14.7 mg/L) was reported from a well in the Jackson Purchase Region.

**Table 20.** Summary of ammonia-nitrogen values (mg/L as N).

| | |
|---|---|
| Measurements | 932 |
| Maximum | 14.7 |
| 75th percentile | < 0.050 |
| Median | < 0.020 |
| 25th percentile | < 0.020 |
| Minimum | 0.000 |
| Interquartile range | na |
| Sites | 146 |
| DEP | 0.110 |
| Sites > 0.110 | 17 |

< means analytical result reported as less than the stated value

DEP: Kentucky Department for Environmental Protection risk-based concentration

More than 94 percent of the reported ammonia-nitrogen concentrations are less than 0.11 mg/L (Fig. 92).

There are relatively few sampled sites in BMU 3. Sites where ammonia-nitrogen concentrations exceed 0.11 mg/L occur in all physiographic regions and all major watersheds (Fig. 93).

The highest reported concentration was from a site in the Jackson Purchase Region; however, the largest number of high concentrations were found in the Western Pennyroyal Region (Fig. 94).

With one exception, reported ammonia-nitrogen concentrations were generally lowest in the Tennessee and Mississippi River watersheds. The highest values are in the Lower Cumberland watershed (Fig. 95).

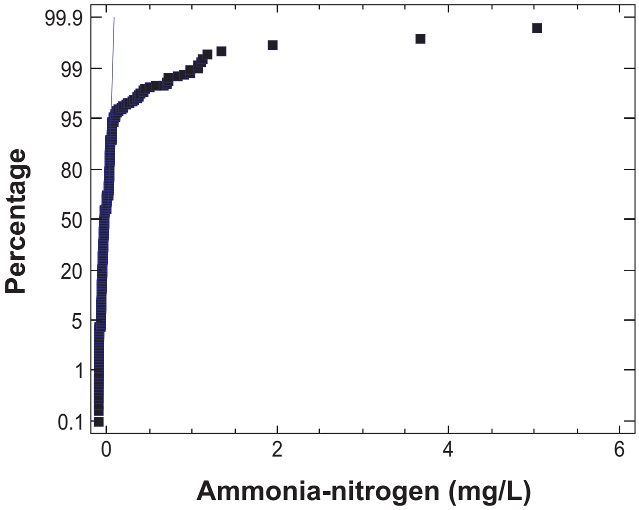

Figure 92. Cumulative plot of ammonia-nitrogen values from BMU 3. The highest value (14.7 mg/L) was omitted to better show the majority of the data.

All analyzed samples were unfiltered (total concentrations), so no comparison of total versus dissolved ammonia-nitrogen can be made. High ammonia-nitrogen values are more commonly found in wells than in springs (Fig. 96) and are more common in shallow wells than in intermediate or deep wells (Fig. 97).

In summary, approximately 11 percent of the sampled wells and springs produced groundwater with more than 0.110 mg/L ammonia-nitrogen. There was no preferred location of such sites, however. The source of ammonia-nitrogen in these groundwaters cannot be established definitely without additional information. Nonpoint-source contributions from agriculture, confined animal feeding operations, or septic systems are certainly possible, however.

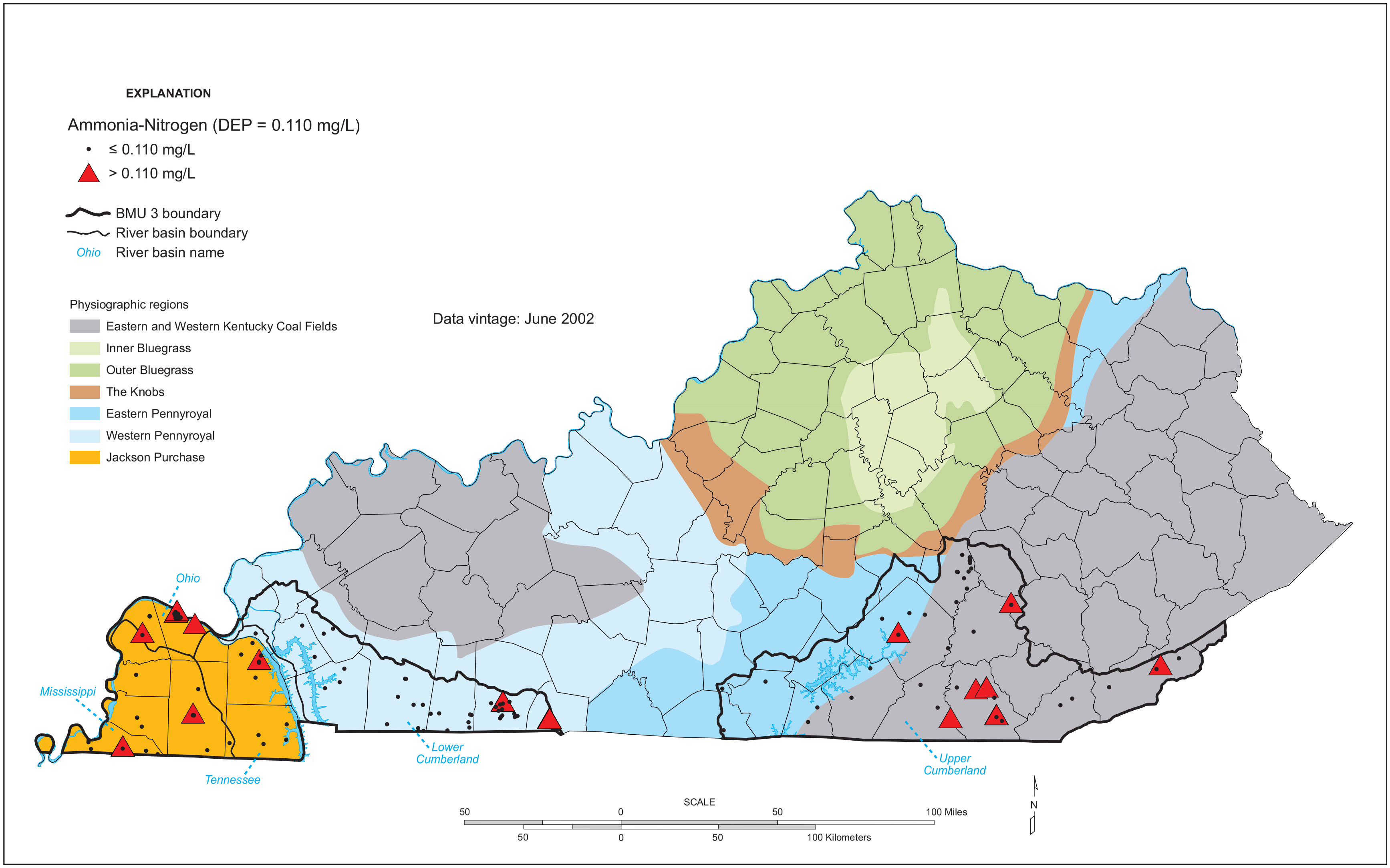

Figure 93. Sample sites and ammonia-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

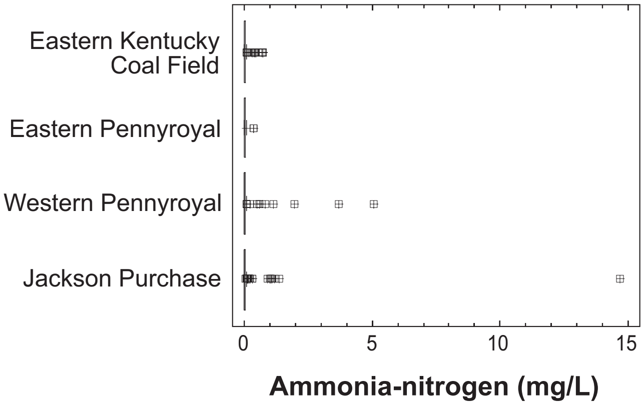

Figure 94. Ammonia-nitrogen data grouped by physiographic region.

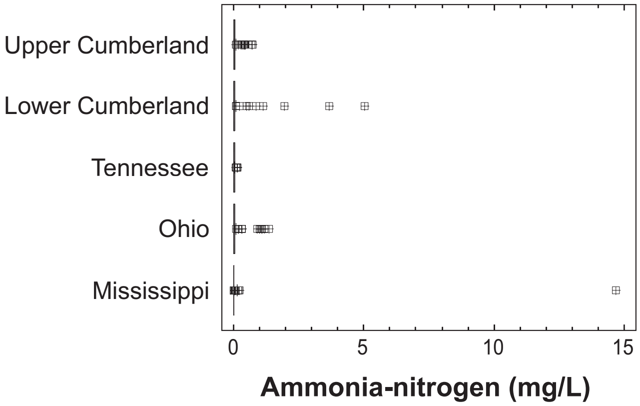

Figure 95. Ammonia-nitrogen data grouped by major watershed.

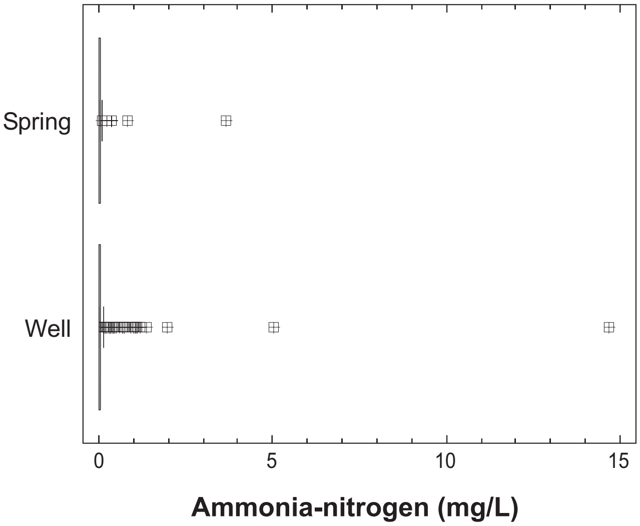

Figure 96. Comparison of ammonia-nitrogen concentrations grouped by site type.

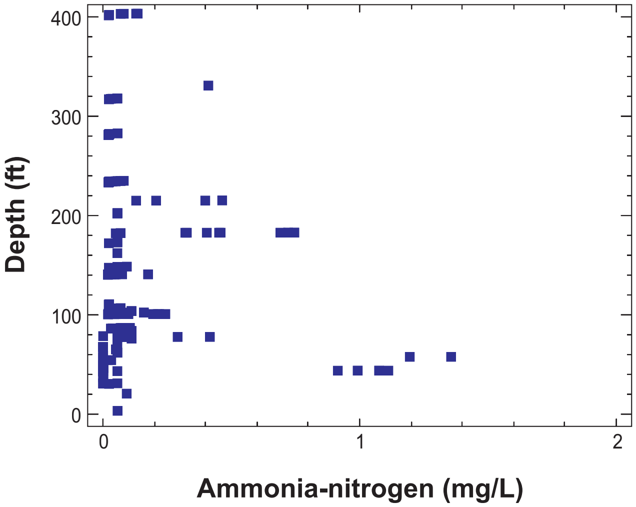

Figure 97. Ammonia-nitrogen concentrations versus well depth.

**Phosphorus Species.** Phosphorus is a common element in the earth's crust, and also is a minor constituent of the carbonate rocks that make up Kentucky's Pennyroyal regions. Most inorganic phosphorus compounds have low solubility, which limits phosphorus concentrations in natural waters. Phosphorus species are readily adsorbed onto soil particles and organic material, which restricts their mobility in nature.

Phosphorus is commonly the limiting nutrient in aquatic ecosystems. The most important man-made sources of phosphorus are phosphate fertilizers, sewage, and animal waste. Prior to the 1960's, phosphate was added to detergents, but this practice was ended because of the eutrophication that resulted when sewage disposal facilities released the water to streams and lakes.

Orthophosphate (complexes containing $PO_4^{-3}$) as $H_2PO_4^{-1}$ or $HPO_4^{-2}$ is the most common form of phosphorus in most natural waters (Hem, 1985). The specific form of orthophosphate is pH-dependent, but normal sample collection and analysis procedures report all phosphate determined on a filtered sample as total orthophosphate. Phosphorus can also occur as organic particulate material. Reports of "total" or "total extractable" phosphorus that result from analysis of unfiltered water samples generally include both dissolved orthophosphate and particulate phosphorus. In groundwater samples, the difference between phosphorus reported as total orthophosphate and total phosphorus is usually because of particulate organic phosphorus.

There are no health-based water-quality standards for orthophosphate; however, the Kentucky Division of Water recommends that orthophosphate concentrations be less than 0.04 mg/L $PO_4$-P based on the Texas surface-water standard.

*Orthophosphate.* The data repository contained 170 orthophosphate measurements from 67 sites in BMU 3 (Table 21). Of those 170 measurements, 153 were reported as below a detection limit, and 123 were reported as less than 0.059 mg/L. Whether these 123 values exceeded the recommended water-quality standard cannot be determined. Only 13 measurements at 10 sites are known to exceed the water-quality standard in BMU 3.

Most measured orthophosphate follows a normal distribution curve (Fig. 98).

Figure 99 shows a fairly uniform but sparse distribution of sample sites. Sites where measured orthophosphate-P concentrations exceed 0.04 mg/L occur in the Upper Cumberland River watershed (Eastern Kentucky Coal Field Region), the Lower Cumberland River watershed (Western Pennyroyal Region), and the Ohio River watershed (Jackson Purchase Region).

**Table 21.** Summary of orthophosphate-P values (mg/L).

| | |
|---|---|
| Measurements | 170 |
| Maximum | 0.495 |
| 75th percentile | < 0.059 |
| Median | < 0.059 |
| 25th percentile | < 0.059 |
| Minimum | < 0.019 |
| Interquartile range | na |
| Sites | 67 |
| DOW | 0.04 |
| Sites > 0.04 | 10 |

< means analytical result reported as less than the stated value
DOW: Kentucky Division of Water recommended value

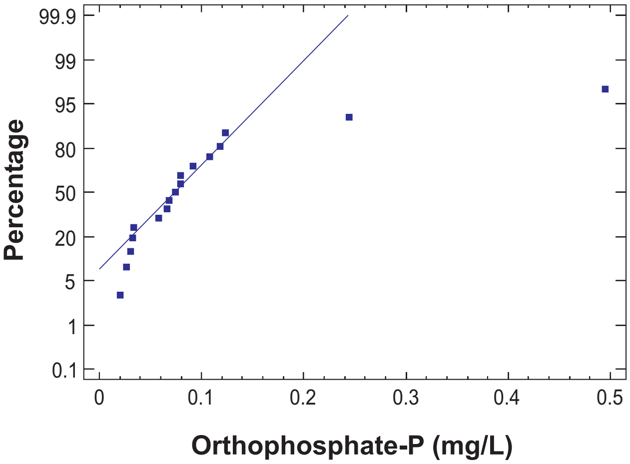

Figure 98. Cumulative plot of orthophosphate values in BMU 3. Values reported as less than a detection limit are excluded.

As was the case for other nutrients, higher orthophosphate concentrations are more likely to be reported from wells than from springs (Fig. 100). Because of the very small number of measured values, no relation between orthophosphate and depth is apparent (Fig. 101).

In summary, more than three-fourths of the orthophosphate-phosphorus measurements in BMU 3 were reported as less than a detection limit of 0.059 mg/L. Many of these were probably below the recommended water-quality standard of 0.04 mg/L, but the exact number cannot be determined. Only 10 sites yielded groundwater with measured orthophosphate-phosphorus concentrations that exceeded the water-quality standard. Nonpoint-source contributions of orthophosphate nutrients to groundwater cannot be evaluated in BMU 3 at this time because of the very small number of accurate measurements.

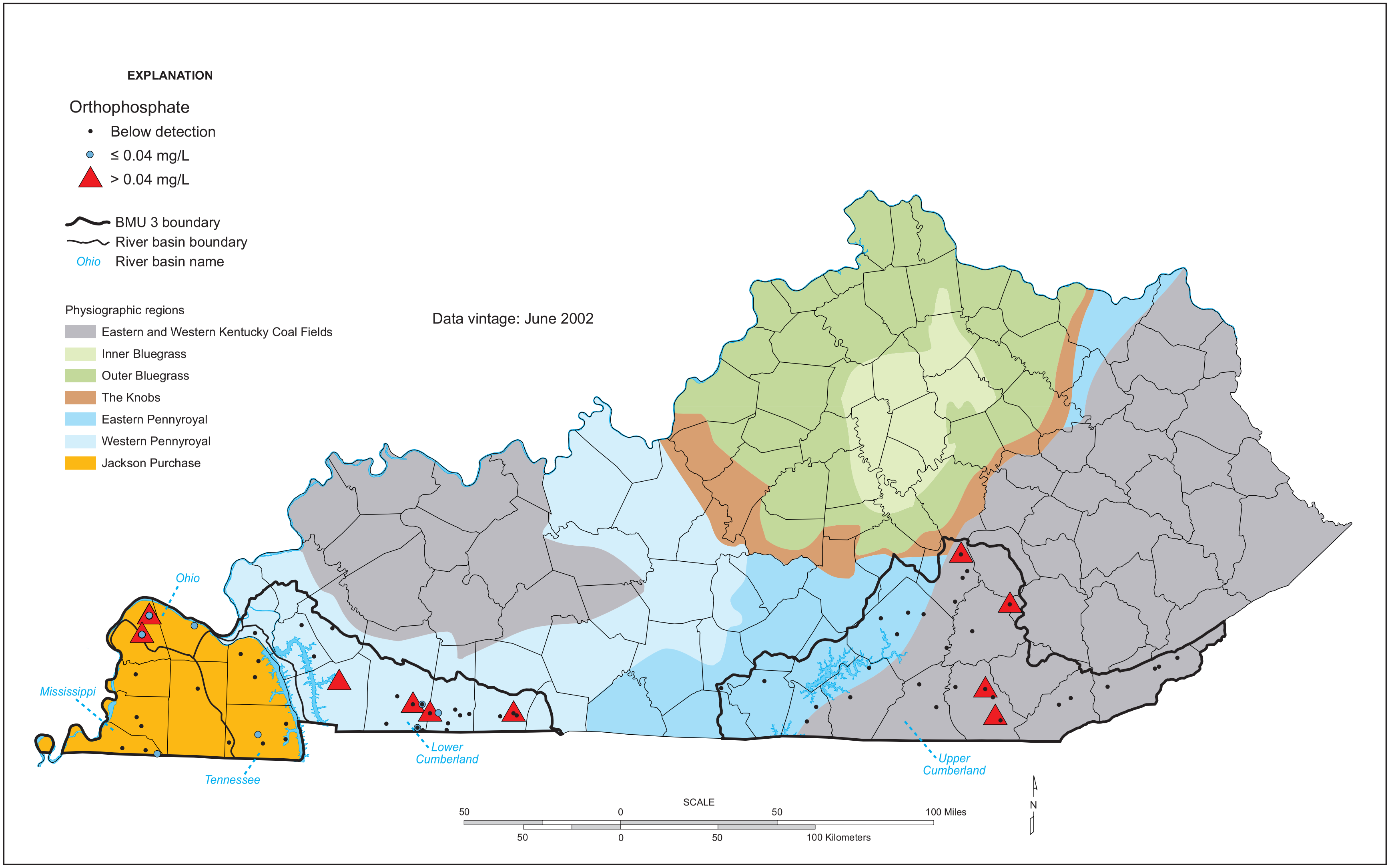

Figure 99. Sample sites and orthophosphate-P values. Superimposed symbols indicate that values recorded at different collection times fell into different ranges.

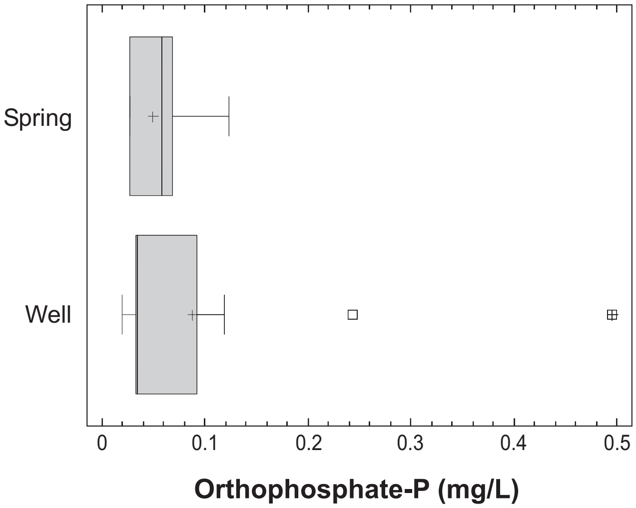

Figure 100. Comparison of orthophosphate values from springs and wells. Values below detection limits are not plotted.

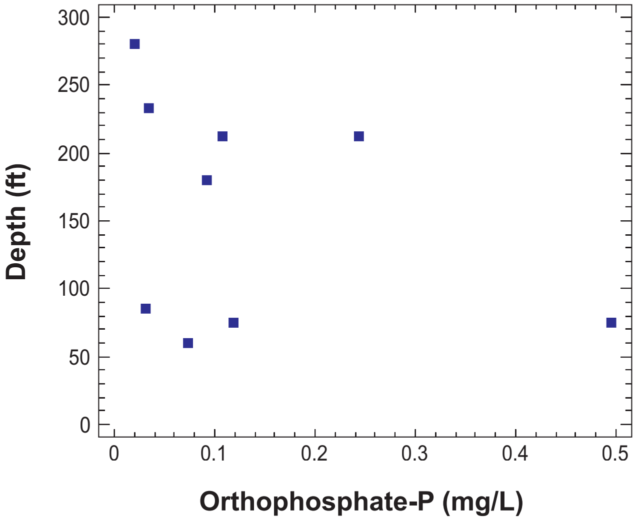

Figure 101. Orthophosphate values versus well depth. Values below detection limits are not plotted.

*Total Phosphorus.* The database contained 443 reports of total phosphorus at 48 sites (Table 22). The maximum reported total phosphorus measurement was 93.6 mg/L from a well in the Upper Cumberland River watershed, in the Eastern Pennyroyal Region. Because the second highest reported value was only 3.3 mg/L, the maximum value is considered anomalous and is not included in the following discussion.

**Table 22.** Summary of total phosphorus values (mg/L).

| | |
|---|---|
| Measurements | 443 |
| Maximum | 93.92 |
| 75th percentile | < 0.08 |
| Median | 0.024 |
| 25th percentile | 0.008 |
| Minimum | 0.005 |
| Interquartile range | na |
| Sites | 48 |
| DOW | 0.1 |
| Sites > 0.1 | 22 |

< means analytical result reported as less than the stated value
DOW: Kentucky Division of Water recommended value

The Division of Water has proposed a value of 0.1 mg/L as the groundwater-quality standard, based on information from the U.S. Geological Survey National Water-Quality Assessment Program. Twenty-two sites in BMU 3 yielded groundwater that exceeded 0.1 mg/L total phosphorus. Three sites accounted for a total of 44 analyses that were reported as less than a detection limit of 0.12 mg/L; that is, less than a detection limit that is greater than the value of interest (0.1 mg/L). One of these sites had also produced a sample having a total phosphorus concentration greater than 0.1 mg/L. For the other two sites, analytical results of "less than 0.12 mg/L" are the only entries in the database. Whether the actual total phosphorus concentrations at these sites were less than the recommended value of 0.1 mg/L cannot be determined.

The data distribution is not normal (Fig. 102). Approximately 95 percent of the values follow a normal distribution from 0.0 to about 0.1 mg/L, but there is also a small group of much higher values.

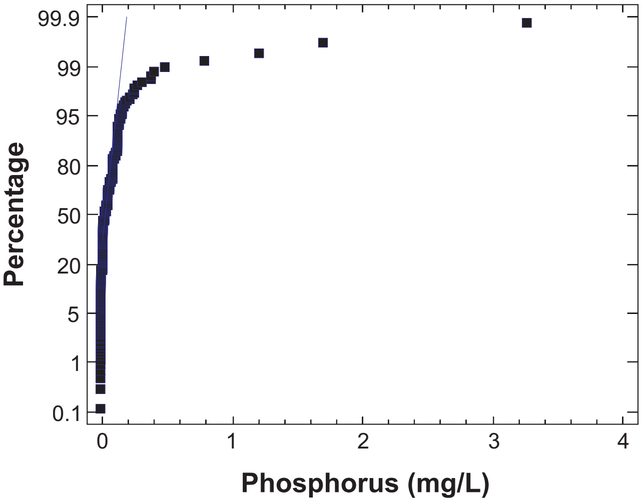

Figure 102. Cumulative plot of total phosphorus values.

Sample sites are well distributed throughout the project area (Fig. 103). Sites where total phosphorus exceeds 0.1 mg/L occur in all physiographic regions (Figs. 104–105) and all major watersheds except that of the Ohio River (Figs. 103 and 105).

High total phosphorus concentrations are more common in wells than in springs (Fig. 106), and more common in wells less than 100 ft deep than in deeper wells (Fig. 107).

In summary, total phosphorus concentrations that exceed the recommended value of 0.1 mg/L were reported throughout BMU 3. Such sites are widespread throughout the Eastern Kentucky Coal Field, areally restricted in the Western Pennyroyal Region, and isolated in the Jackson Purchase. Shallow wells are more likely to produce groundwater with total phosphorus concentrations above 0.1 mg/L than deep wells or springs. Nonpoint-source contributions of total phosphorus to groundwater are probably minor compared to natural sources in the coal fields and the carbonate Pennyroyal regions. That shallow wells are most likely to produce groundwater having high phosphorus concentrations suggests, however, that there may be a nonpoint-source contribution.

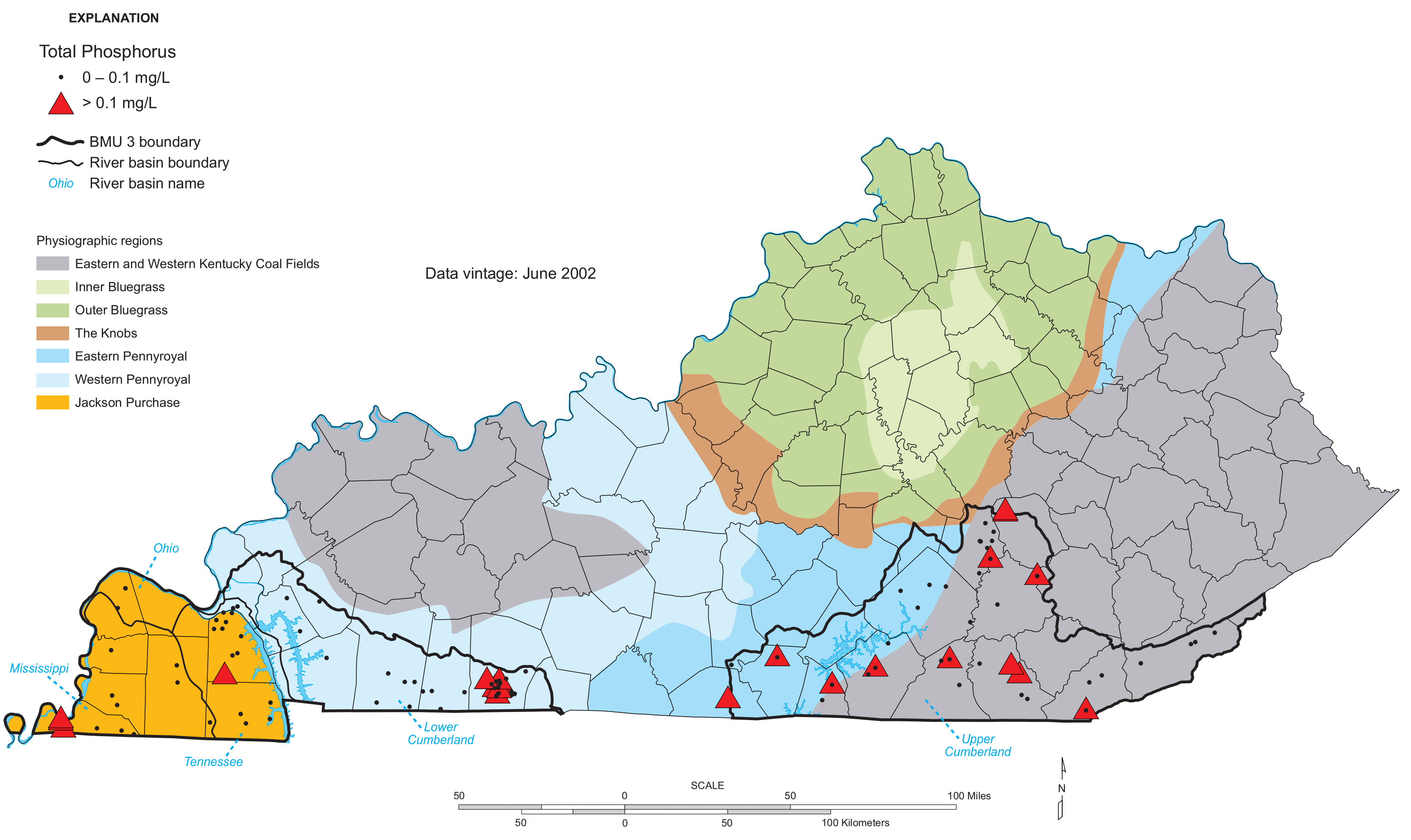

Figure 103. Sample sites and ranges of total phosphorus values. Superimposed symbols indicate that values measured at the same site but at different sampling times fell into different ranges.

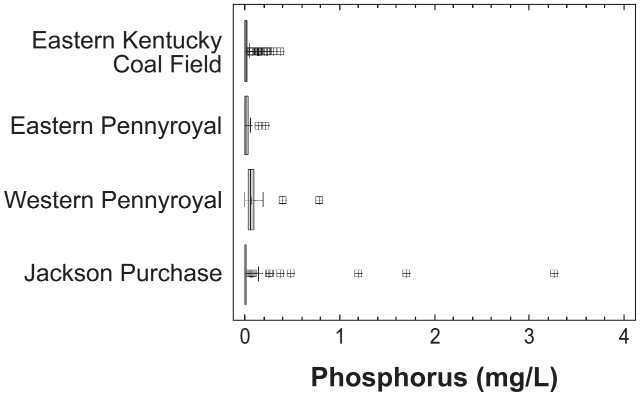

Figure 104. Summary of total phosphorus values grouped by physiographic region.

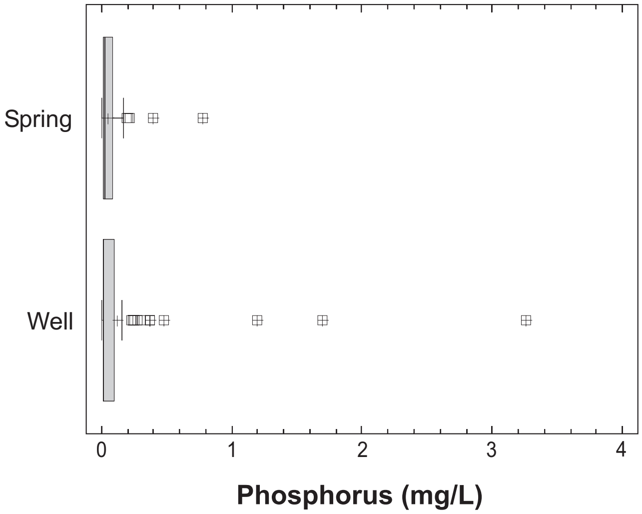

Figure 106. Comparison of total phosphorus values from wells and springs.

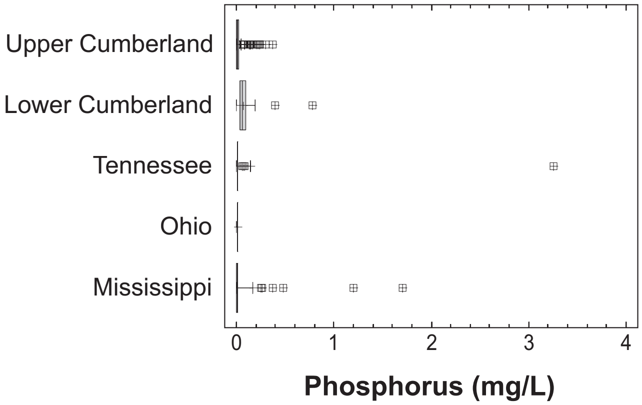

Figure 105. Total phosphorus values grouped by major watershed.

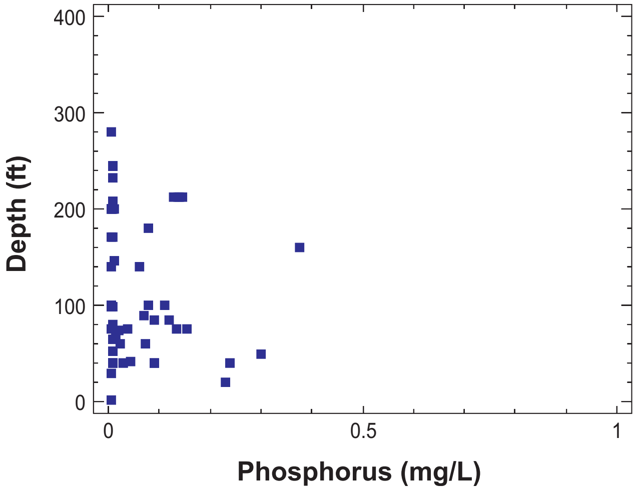

Figure 107. Total phosphorus concentrations versus well depth.

# Pesticides

A large number of synthetic organic pesticides (including insecticides, herbicides, and growth regulators) have been developed and applied in agricultural and urban settings. Some, such as the organochlorine insecticide DDT, were banned decades ago but still persist in soils and sediments and could still be released to groundwater systems. Most recently developed pesticides that have been approved for use are less persistent in natural environments; however, they may still have undesirable impacts on human health and groundwater suitability for various uses.

The environmental significance of pesticides in groundwater is difficult to determine precisely for several reasons (U.S. Geological Survey, 1999): (1) standards and guidelines are available for only a small number of individual pesticide chemicals and are generally not available for the equally important degradation products, (2) new pesticides are being developed continually, (3) environmental testing does not account for pesticide mixtures or breakdown products, which may be more potent than the original active ingredients, (4) only a limited suite of health and ecological effects have been tested, (5) concentrations much higher than those used in testing may be introduced to groundwater systems when pesticides are applied or after rains, and (6) some detrimental effects such as endocrine disruption and other subtle health effects have not been fully assessed. For these reasons, and because once contaminated, groundwater typically is slow to respond to changes in pesticide type and application methods, quantifying the existence of any detectable pesticides in Kentucky groundwater is important.

According to the 2000 agriculture sales data, atrazine, glyphosate, metolachlor, simazine, and 2,4-D are the top five pesticides sold in Kentucky. Alachlor and cyanazine have also been used extensively in the past. Glyphosate has not been measured in groundwater samples and so will not be discussed in this report. Toxicological information for pesticides was obtained from the Extension Toxicology Network and is available on the Web site ace.orst.edu/info/extoxnet.pips/.

**2,4-D.** The pesticide 2,4-D belongs to the chemical class of phenoxy compounds. Predominant uses are as a systemic herbicide to control broadleaf weeds in cultivated agriculture, pasture and range land, forest management, home and garden settings, and to control aquatic vegetation.

It has a low persistence in soils with a half-life of less than 7 days, and is readily degraded by microorganisms in aquatic environments. The EPA has established an MCL of 0.07 mg/L for 2,4-D.

The data repository contained 516 measurements of 2,4-D from 117 sites (Table 23). In BMU 3, 510 of 516 measurements (98.8 percent) were reported as less than a detection limit. No site yielded groundwater with 2,4-D concentrations above the MCL. Only three sites had detectable levels of 2,4-D (Fig. 108). All sites where 2,4-D was detected are springs; no 2,4-D was found in well samples. No cumulative data distribution plots or further analyses were performed because there were so few measurements above the detection limit of the analytical method.

**Table 23.** Summary of 2,4-D values (mg/L).

| | |
|---|---|
| Measurements | 516 |
| Maximum | < 0.0009 |
| 75th percentile | < 0.000335 |
| Median | < 0.0001 |
| 25th percentile | < 0.0001 |
| Minimum | 0.00001 |
| Interquartile range | na |
| Sites | 117 |
| MCL | 0.07 |
| Sites > 0.07 | 0 |

< means analytical result reported as less than the stated value

In summary, the pesticide 2,4-D was detected at three of 117 sites; all detections were in groundwater from springs. No samples had 2,4-D concentrations greater than the MCL of 0.07 mg/L. The observed occurrences, coupled with the short half-life, suggest that 2,4-D degrades in the time it takes to travel from application site to water wells. Rapid runoff can transport 2,4-D to springs, however, where the water might be consumed or used for other domestic purposes.

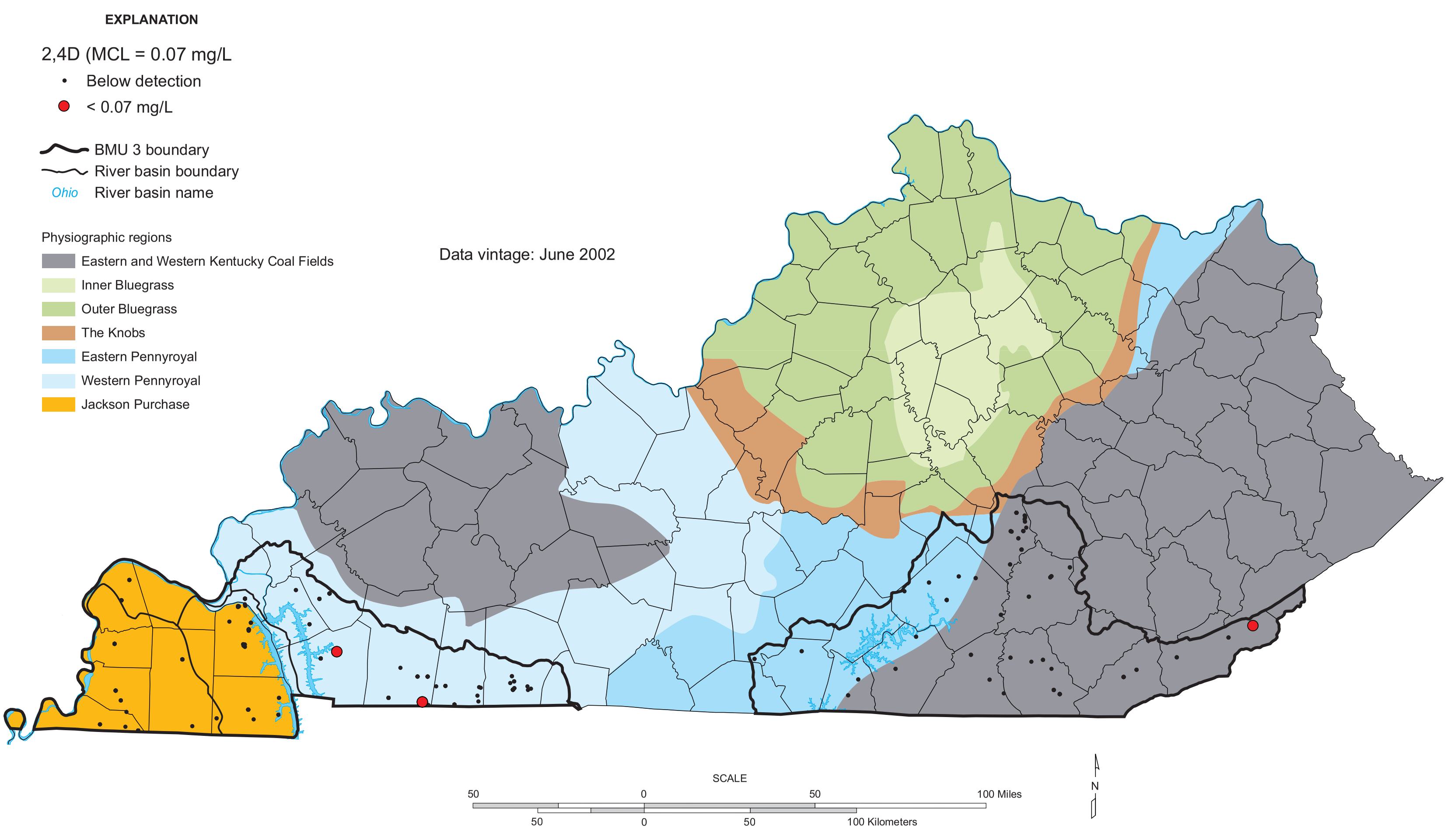

Figure 108. Locations of sites where 2,4-D was measured and ranges of 2,4-D values. No sites exceeded the MCL.

**Alachlor.** Alachlor belongs to the chemical class of analines. Predominant uses are the control of annual grasses and broadleaf weeds in field corn, soybeans, and peanuts. It has a low persistence in soils and half-life of about 8 days. It is moderately mobile in sandy and silty soils and breaks down rapidly in natural water because of microbial activity. The breakdown is significantly slower under reducing conditions. The EPA has set an MCL of 0.002 mg/L for alachlor.

The data repository contained 2,413 results of analyses from 107 sites (Table 24). Of the 2,413 measurements, 1,078 were reported from a single site, and 1,543 of the measurements (63.9 percent) were reported as less than a detection limit.

Cumulative data distributions were not plotted because of the small number of measurements above analytical detection limits.

The site distribution is relatively even but sparse throughout the project area. Two sites in the Lower Cumberland River watershed of the Western Pennyroyal Region yielded groundwater with alachlor concentrations above the MCL (Fig. 109). Twenty sites, most of them in the Lower Cumberland River watershed of the Western Pennyroyal Region, had detectable levels of alachlor.

**Table 24.** Summary of alachlor values (mg/L).

| | |
|---|---|
| Measurements | 2,413 |
| Maximum | 0.01200 |
| 75th percentile | 0.00010 |
| Median | < 0.00006 |
| 25th percentile | < 0.00006 |
| Minimum | < 0.00002 |
| Interquartile range | na |
| Sites | 107 |
| MCL | 0.002 |
| Sites > 0.002 | 2 |

< means analytical result reported as less than the stated value

Only three of the sites where alachlor was detected are water wells; the remainder are springs or are part of a karst system. Nearly all of the alachlor measurements that were above detection limits were from

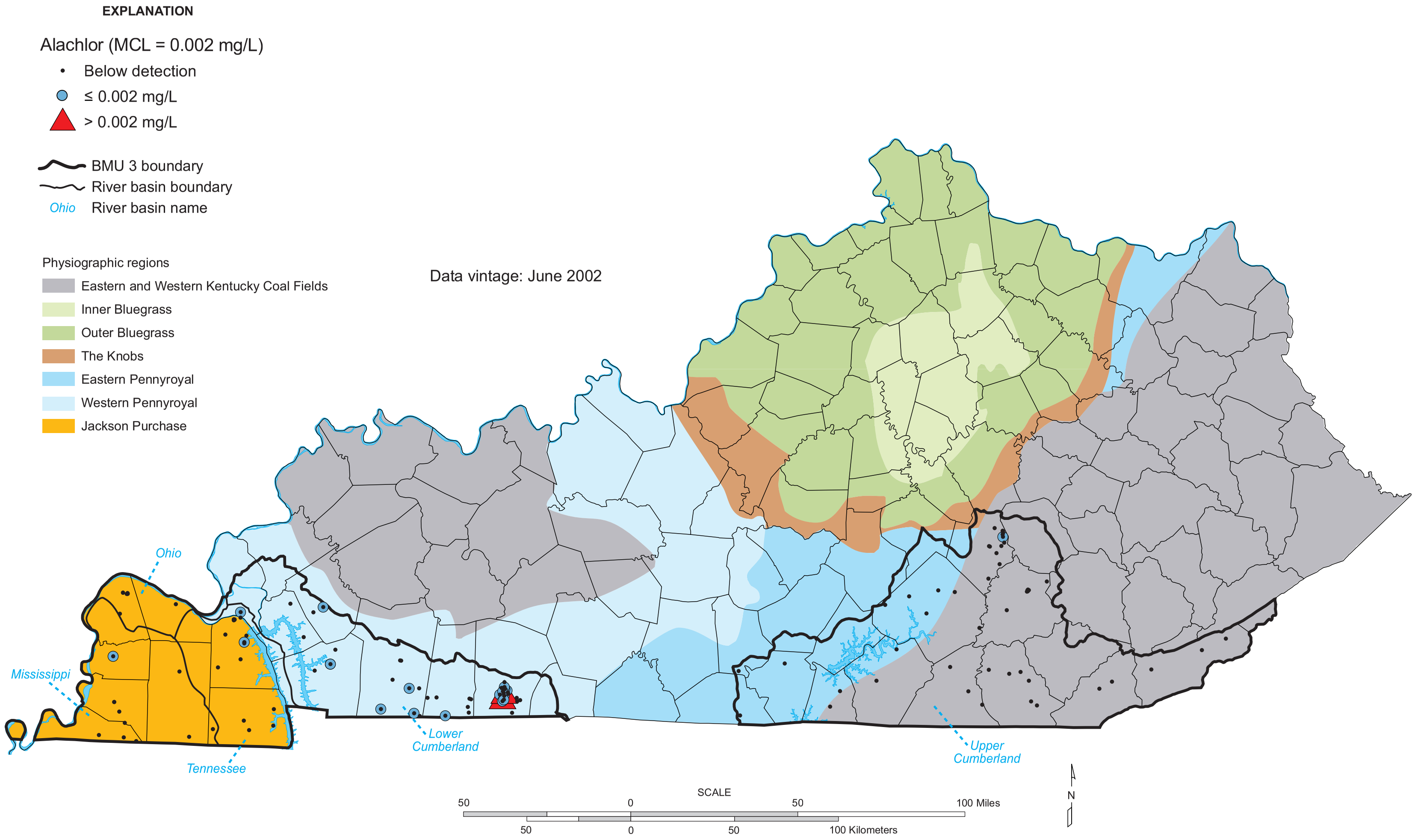

Figure 109. Locations of sites where alachlor was measured and ranges of alachlor values.

springs rather than wells (Fig. 110). An analysis of the relation between well depth and alachlor concentration was not possible because very few well samples had both detectable alachlor and a recorded well depth.

In summary, alachlor exceeded the MCL at two sites. It was detected at 20 of 107 sites, most of which were springs in karst systems. Alachlor apparently degrades before reaching most water wells, but can be transported through springs rapidly enough to persist at potentially harmful levels.

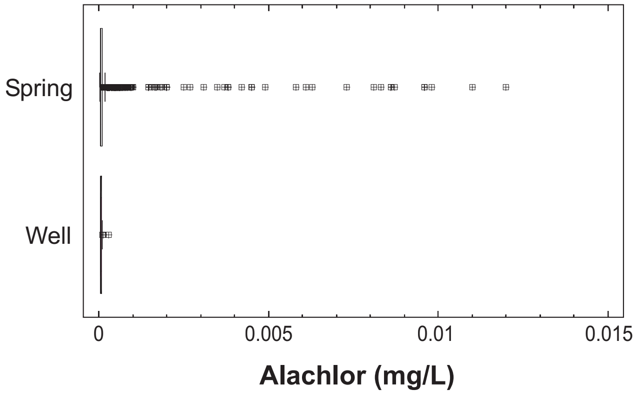

Figure 110. Comparison of alachlor values in wells and springs.

**Atrazine.** Atrazine belongs to the chemical class of triazines. Predominant uses are to control broadleaf and grassy weeds in corn, sorghum, and other crops and in conifer reforestation plantings. It is highly persistent in soils, moderately soluble in water, and not readily sorbed to sediments. The EPA has set an MCL of 0.003 mg/L for atrazine.

The data repository contained 638 analytical reports of atrazine from 62 sites (Table 25). In BMU 3, 400 of 638 measurements were reported as less than a detection limit. Atrazine concentrations were above analytical detection limits at 21 sites and exceeded the MCL at four sites.

**Table 25.** Summary of atrazine values (mg/L).

| | |
|---|---|
| Measurements | 638 |
| Maximum | 0.039 |
| 75th percentile | 0.00042 |
| Median | < 0.0003 |
| 25th percentile | 0.00006 |
| Minimum | 0.00002 |
| Interquartile range | 0.0004 |
| Sites | 62 |
| MCL | 0.003 |
| Sites > 0.003 | 4 |

< means analytical result reported as less than the stated value

Few sites in the Upper Cumberland River watershed were sampled for atrazine (Fig. 111), and none of these sites had atrazine values above the MCL. Sample site distribution is sparse in the Lower Cumberland River watershed and Jackson Purchase Region. All sites where atrazine exceeded the MCL are located in the carbonate terrain of the Western Pennyroyal Region, in the Lower Cumberland River watershed.

Groundwater from springs yields more high-atrazine measurements than does groundwater from wells, and springs are the only sites where atrazine concentrations exceed the 0.003 mg/L MCL (Fig. 112). Atrazine concentrations above analytical detection limits have been found in wells as deep as 200 ft, but no groundwater from wells had an atrazine concentration greater than the MCL (Fig. 113).

In summary, four sites in the project area produced groundwater that exceeded the MCL for atrazine; 21 of 62 sites produced groundwater with atrazine concentrations greater than the analytical detection limit. Springs are more likely than wells to have relatively high atrazine levels, and shallow wells are more likely than deep wells to have relatively high atrazine concentrations. The data suggest that atrazine in the subsurface is degraded to the low levels observed in wells. Rapid runoff from fields to springs allows high atrazine concentrations to contaminate springs, however.

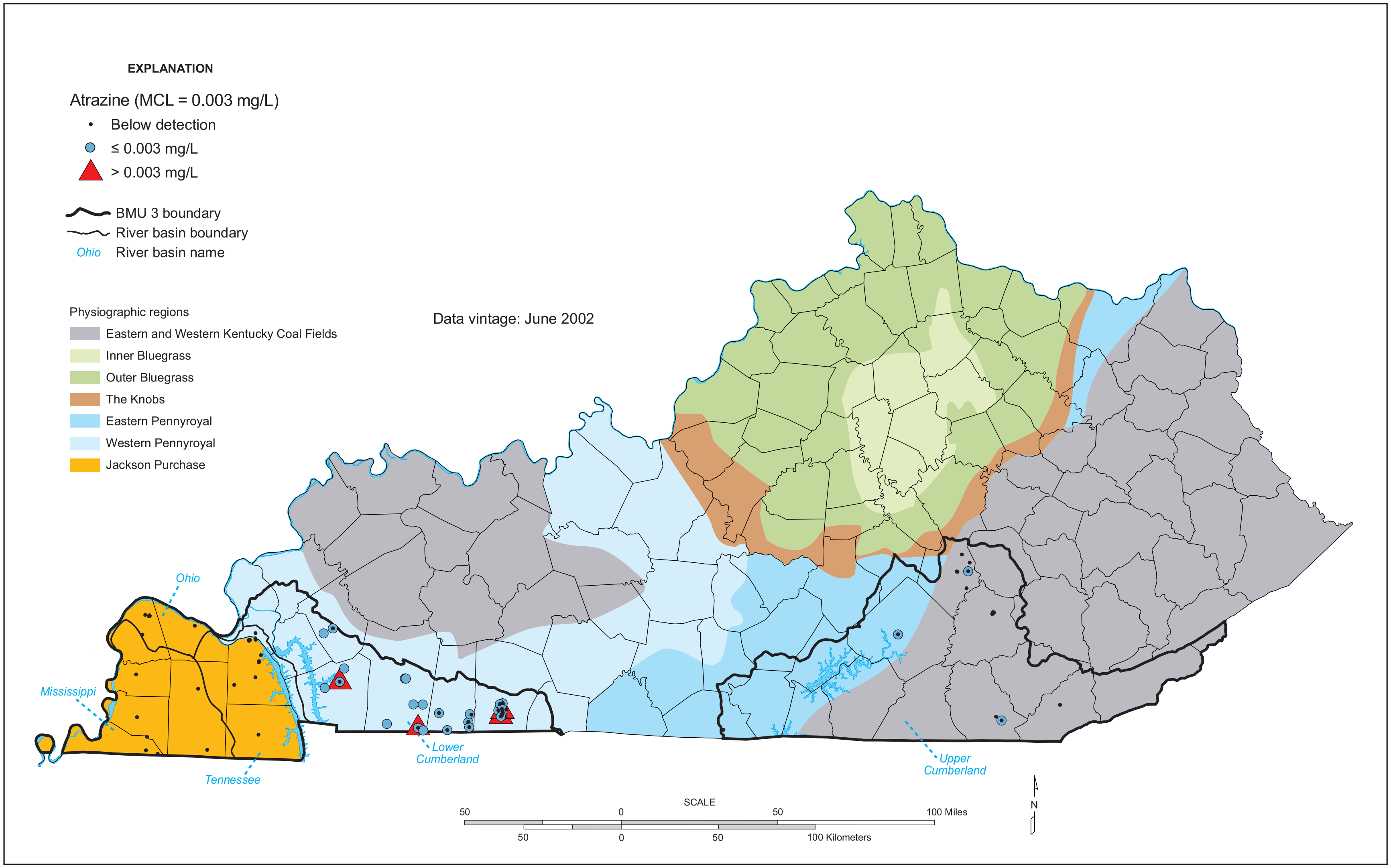

Figure 111. Locations of sites where atrazine was measured and ranges of atrazine values.

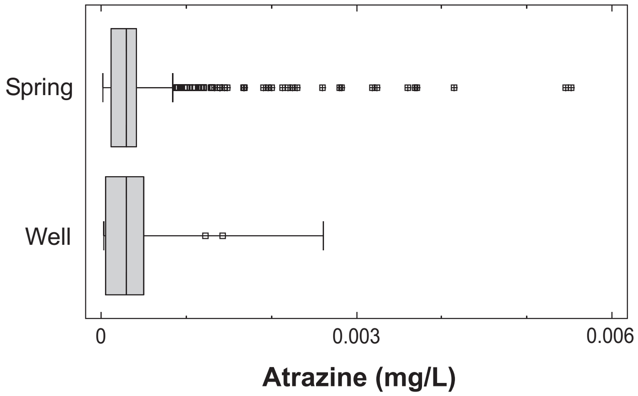

Figure 112. Comparison of atrazine values from wells and springs.

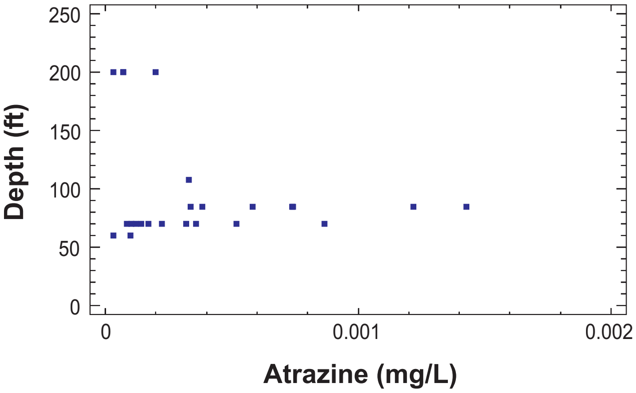

Figure 113. Atrazine concentrations versus well depth. Only results that exceeded analytical detection limits are shown.

**Cyanazine.** Cyanazine belongs to the chemical class of triazines. It is used mainly to control annual grasses and broadleaf weeds in corn. It has low to moderate persistence in soils and is rapidly degraded by microbial activity. Cyanazine has a half-life of 2 to 14 weeks, depending on soil type, and is stable in water. There is no MCL for cyanazine. The Division of Water has set a health advisory limit (HAL) of 0.001 mg/L.

The data repository contained 489 reports of cyanazine analyses at 97 sites (Table 26). Only four measurements at three sites exceeded analytical detection limits. Groundwater from springs in the Lower Cumberland River watershed of the Western Pennyroyal Region accounted for all the samples in which cyanazine was present at detectable concentrations (Fig. 114). One spring in the Lower Cumberland River watershed of the Western Pennyroyal Region produced groundwater with a cyanazine concentration that exceeded the HAL of 0.001 mg/L. Because of the very small number of cyanazine detections, no further analysis was performed.

**Table 26.** Summary of cyanazine values (mg/L).

| | |
|---|---|
| Measurements | 489 |
| Maximum | 0.00440 |
| 75th percentile | < 0.00010 |
| Median | < 0.00005 |
| 25th percentile | < 0.00004 |
| Minimum | < 0.00004 |
| Interquartile range | na |
| Sites | 97 |
| HAL | 0.001 |
| Sites > 0.001 | 1 |

< means analytical result reported as less than the stated value

In summary, cyanazine is rarely detected in the project area. The highest concentrations were observed in springs in the Lower Cumberland River watershed of the Western Pennyroyal physiographic region.

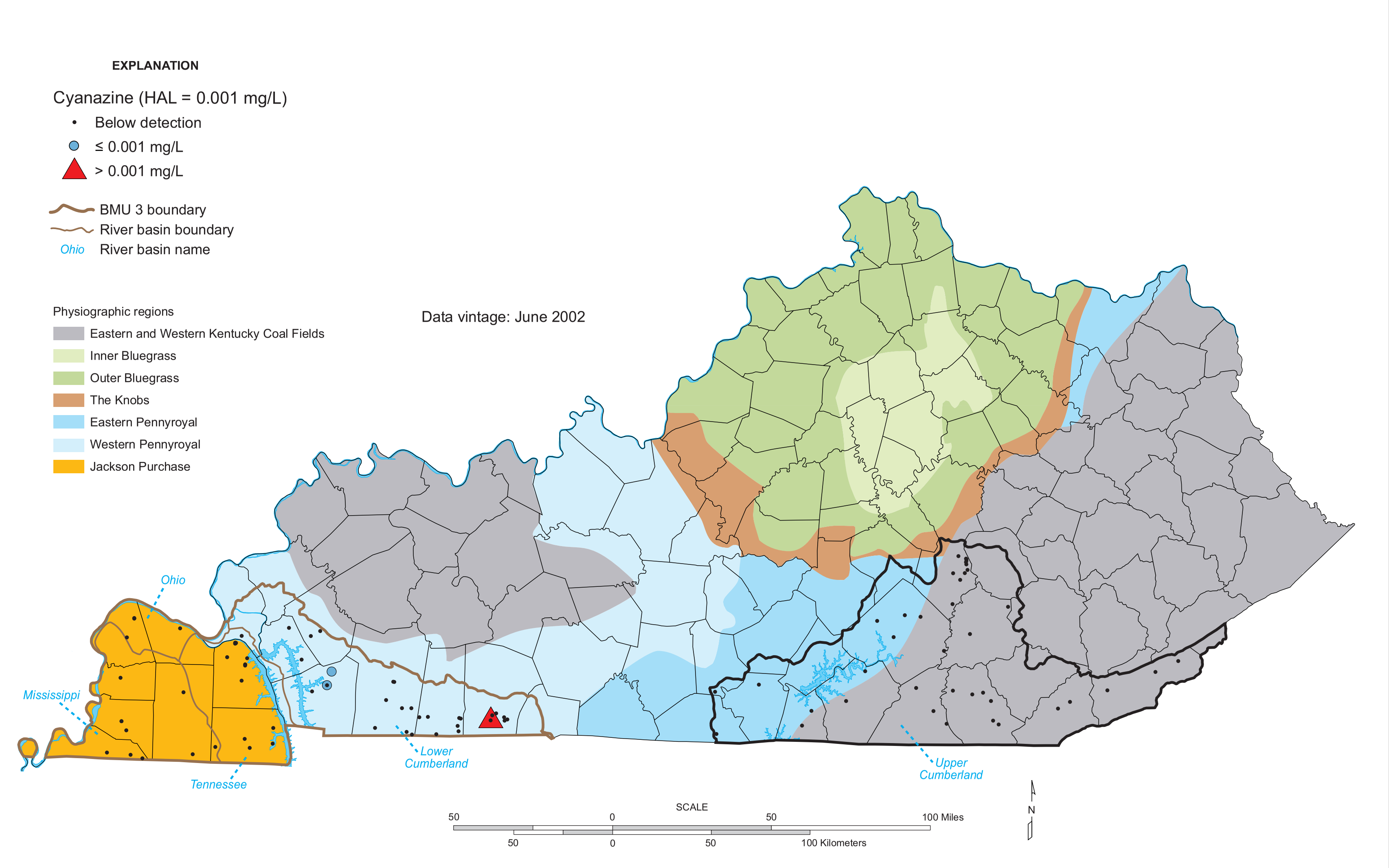

Figure 114. Locations of sites where cyanazine was measured and ranges of cyanazine values.

**Metolachlor.** Metolachlor belongs to the chemical class of amides. It is predominantly used to control broadleaf and grassy weeds in field corn, soybeans, peanuts, grain sorghum, potatoes, pod crops, cotton, safflower, stone fruits, and nut trees, highway rights-of-way, and woody ornamentals. It is moderately persistent in soils with a half-life of 15 to 70 days, and is highly persistent in water. There is no MCL for metolachlor; the Division of Water has set a health advisory limit of 0.1 mg/L.

The data repository contained 2,650 metolachlor measurements from 100 sites (Table 27). Most measurements were below analytical detection (1,247 of 2,650). No sites produced groundwater that exceeded the HAL for metolachlor. Thirty-one of 100 sites produced water that had metolachlor concentrations above the analytical detection limit. One of these sites is in the Upper Cumberland River watershed and one is in the Jackson Purchase Region. The remainder are in the Lower Cumberland and Tennessee River watersheds of the Western Pennyroyal Region (Fig. 115).

The highest metolachlor concentrations were observed in groundwater from springs (Fig. 116). Metolachlor has been detected in wells as deep as about 200 ft (Fig. 117).

**Table 27.** Summary of metolachlor values (mg/L).

| | |
|---|---|
| Measurements | 2,650 |
| Maximum | 0.0296 |
| 75th percentile | 0.00039 |
| Median | 0.00011 |
| 25th percentile | < 0.00008 |
| Minimum | 0.000001 |
| Interquartile range | na |
| Sites | 100 |
| HAL | 0.1 |
| Sites > 0.1 | 0 |

< means analytical result reported as less than the stated value

In summary, more than half of the groundwater samples analyzed for metolachlor had concentrations that were below detection limits. No sample was found to exceed the HAL of 0.1 mg/L. The highest metolachlor concentrations were found in springs and shallow wells. Metolachlor is apparently degraded before reaching intermediate and deep groundwater systems, but can persist long enough to be detected in shallow wells and springs.

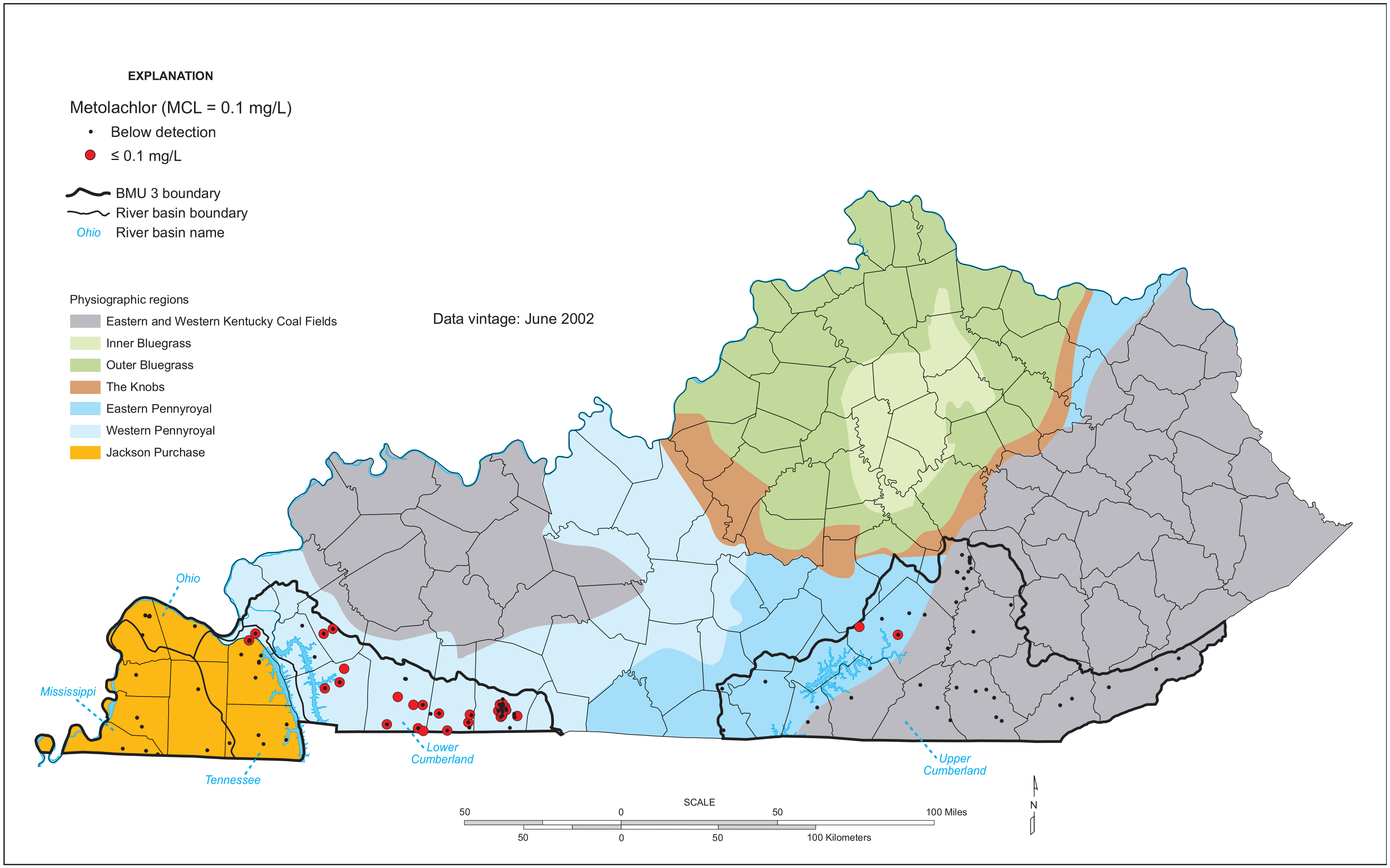

Figure 115. Locations of sites where metolachlor was measured and ranges of metolachlor values.

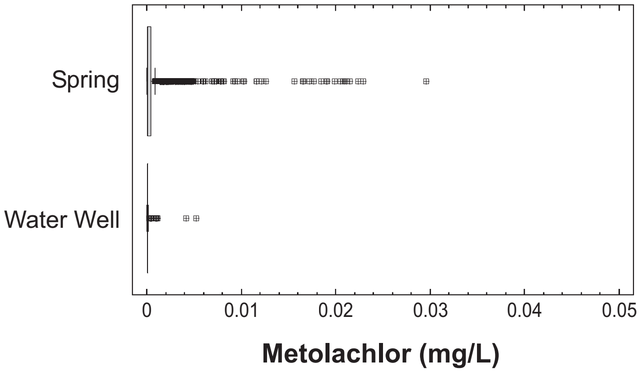

Figure 116. Comparison of metolachlor values in wells and springs.

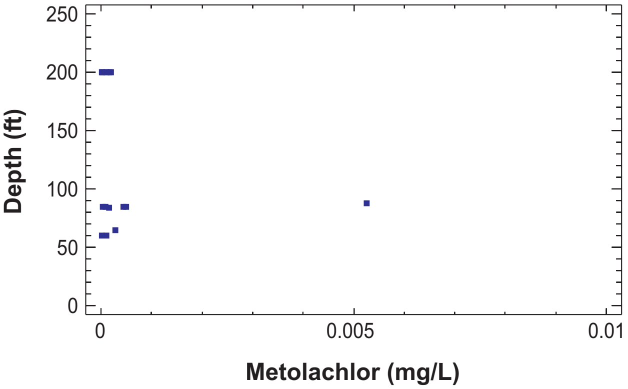

Figure 117. Metolachlor values versus well depth. Only values greater than analytical detection limits are shown.

**Simazine.** Simazine belongs to the chemical class of triazines. It is predominantly used to control broadleaf weeds and annual grasses in fields where berry fruits, nuts, vegetables, and ornamental crops are grown, and on turfgrass. It is moderately persistent in soils, with a half-life of about 60 days, and is moderately persistent in water, with a half-life that depends on the amount of algae present. The MCL for simazine is 0.004 mg/L.

The data repository contained 690 simazine measurements from 99 sites (Table 28). More than 95 percent of the measurements (658 of 690) were below analytical detection limits. Simazine was detected at three wells and 12 springs (Fig. 118). Simazine in groundwater exceeded the MCL at one spring in the Lower Cumberland River watershed of the Western Pennyroyal Region. Simazine concentrations did not vary with well depth. Because of the small number of simazine detections, no further analysis was performed.

**Table 28.** Summary of simazine values (mg/L).

| | |
|---|---|
| Measurements | 690 |
| Maximum | 0.0045 |
| 75th percentile | < 0.0003 |
| Median | < 0.0001 |
| 25th percentile | < 0.00004 |
| Minimum | < 0.00002 |
| Interquartile range | na |
| Sites | 99 |
| MCL | 0.004 |
| Sites > 0.004 | 1 |

< means analytical result reported as less than the stated value

In summary, simazine concentrations exceeded the MCL at one site and were detected at 15 of 99 sites. Twelve of these sites are springs and three are wells. This suggests that rapid transport can carry simazine to springs more readily than to water wells.

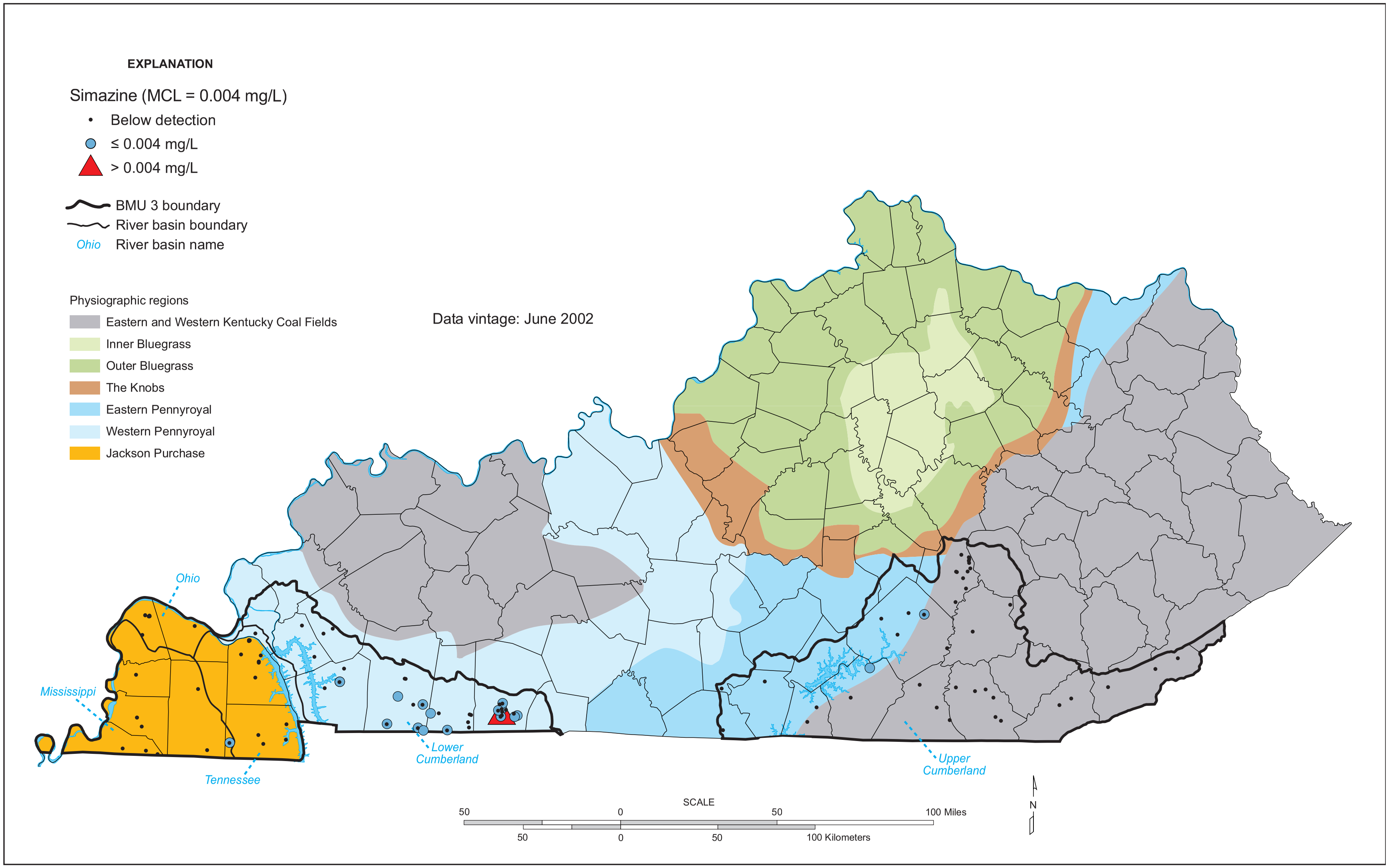

Figure 118. Locations of sites where simazine was measured and ranges of simazine values.

## Volatile Organic Compounds

The volatile organic compounds benzene, ethylbenzene, toluene, and xylene can have serious health effects if they are consumed in drinking water. In addition, MTBE (methyl tert-butyl ether) is a compound of concern, although health threats have not yet been established. Any detected amounts of these refined volatile organic chemicals indicate groundwater contamination. VOC occurrences are not primarily controlled by bedrock geology, physiography, or major river watershed.

Volatile organic compounds may be present in groundwater at very low concentrations. Measurement techniques have improved over time. As a result, some older measurements in the data repository are reported only as less than a detection limit, where the detection limit is larger than some more recently measured values for the same well or spring. In such cases, the maximum value reported in the following tables is the maximum value actually measured, not the value of the detection limit. For example, if two MTBE analyses for a single site are "< 0.02 mg/L" at one time and "0.01 mg/L" at another time, the maximum value reported would be 0.01 mg/L.

Records from monitoring wells (identified by an AKGWA[3] number that begins with "8"; e.g., 80001234) were excluded to avoid any wells drilled to test for leaking underground storage tank contamination. The following summaries of potential sources and health effects of the selected VOC's were taken from the EPA Web page, "Current Drinking Water Standards" (www.epa.gov/safewater/mcl/html) in June 2002.

**Benzene.** The most common sources of benzene in groundwater are leaks from underground gasoline storage tanks and landfills. Potential health effects include anemia, decrease in blood platelets, and increased risk of cancer. For these reasons, EPA has established an MCL of 0.005 mg/L for benzene.

The data repository contained 425 benzene measurements from 224 sites in BMU 3 (Table 29). Fifteen measurements at 10 sites were above analytical detection limits. Benzene concentrations exceeded the MCL at two sites.

Benzene was detected in groundwater in all physiographic regions except the Eastern Pennyroyal (Fig. 119). The two sites where benzene exceeded the MCL are in the Ohio River watershed of the Jackson Purchase (Fig. 119). The small number of measurements that exceed analytical detection limits precludes further data analysis. No relation between benzene concentration and well depth was observed; however, most samples were taken from springs, and few of the sampled wells had a depth recorded. The deepest well in which benzene was found at levels above analytical detection was 185 ft deep.

In summary, occurrences of detectable benzene in groundwater are rare in the project area. Springs are more susceptible to benzene contamination than wells; however, benzene was detected in a well that is 185 ft deep. The presence of detectable amounts of benzene in groundwater confirms some contamination by nonpoint sources or unidentified underground storage tanks.

**Table 29.** Summary of benzene values (mg/L).

| | |
|---|---|
| Measurements | 425 |
| Maximum | 0.01 |
| 75th percentile | < 0.001 |
| Median | < 0.0005 |
| 25th percentile | < 0.0005 |
| Minimum | < 0.0005 |
| Interquartile range | na |
| Sites | 224 |
| MCL | 0.005 |
| Sites > 0.005 | 2 |

< means analytical result reported as less than the stated value

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[3] Assembled Kentucky Ground Water Database

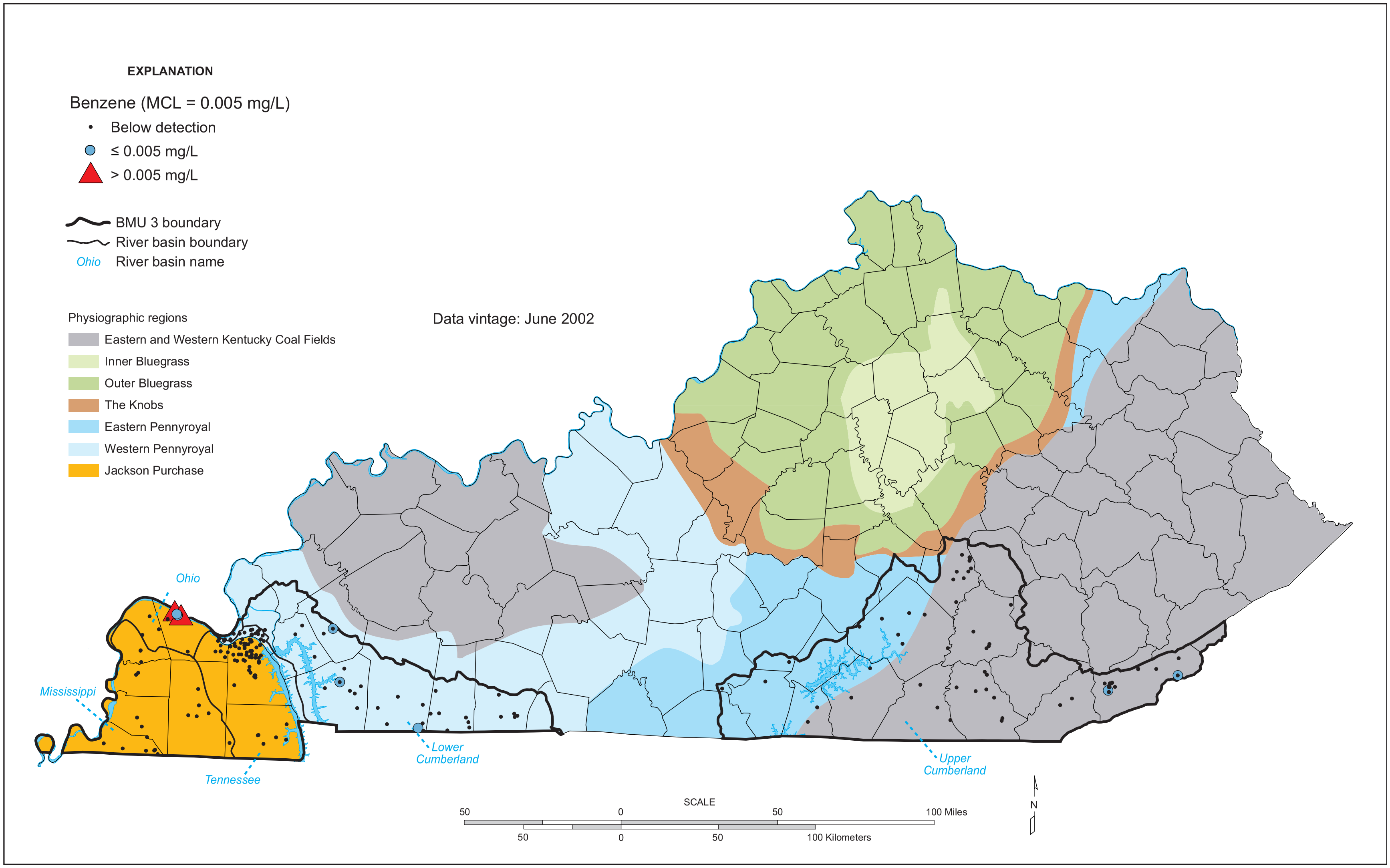

Figure 119. Sample sites and ranges of benzene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

**Ethylbenzene.** Common sources of ethylbenzene are discharge from petroleum refineries and leaking underground gasoline storage tanks. The potential health effects include liver or kidney damage. The EPA has set an MCL for ethylbenzene of 0.7 mg/L.

The data repository contained 425 ethylbenzene measurements at 224 sites (Table 30). Ethylbenzene concentrations exceeded analytical detection limits at eight sites. Three of these are springs in the Lower Cumberland River watershed of the Western Pennyroyal Region; four are shallow (less than 60 ft deep) wells in the Ohio River watershed of the Jackson Purchase, and one is a well of unreported depth in the Upper Cumberland River watershed of Eastern Kentucky Coal Field. Ethylbenzene did not exceed the MCL in the project area (Fig. 120).

**Table 30.** Summary of ethylbenzene values (mg/L).

| | |
|---|---|
| Measurements | 425 |
| Maximum | 0.0706 |
| 75th percentile | < 0.001 |
| Median | < 0.0005 |
| 25th percentile | < 0.0005 |
| Minimum | < 0.0005 |
| Interquartile range | na |
| Sites | 224 |
| MCL | 0.7 |
| Sites > 0.7 | 0 |

< means analytical result reported as less than the stated value

In summary, detectable levels of ethylbenzene in groundwater are rare in the project area and occur in both springs and shallow wells. The small number of occurrences precludes further data analysis. Any detection of ethylbenzene indicates some contamination of the groundwater resource, however.

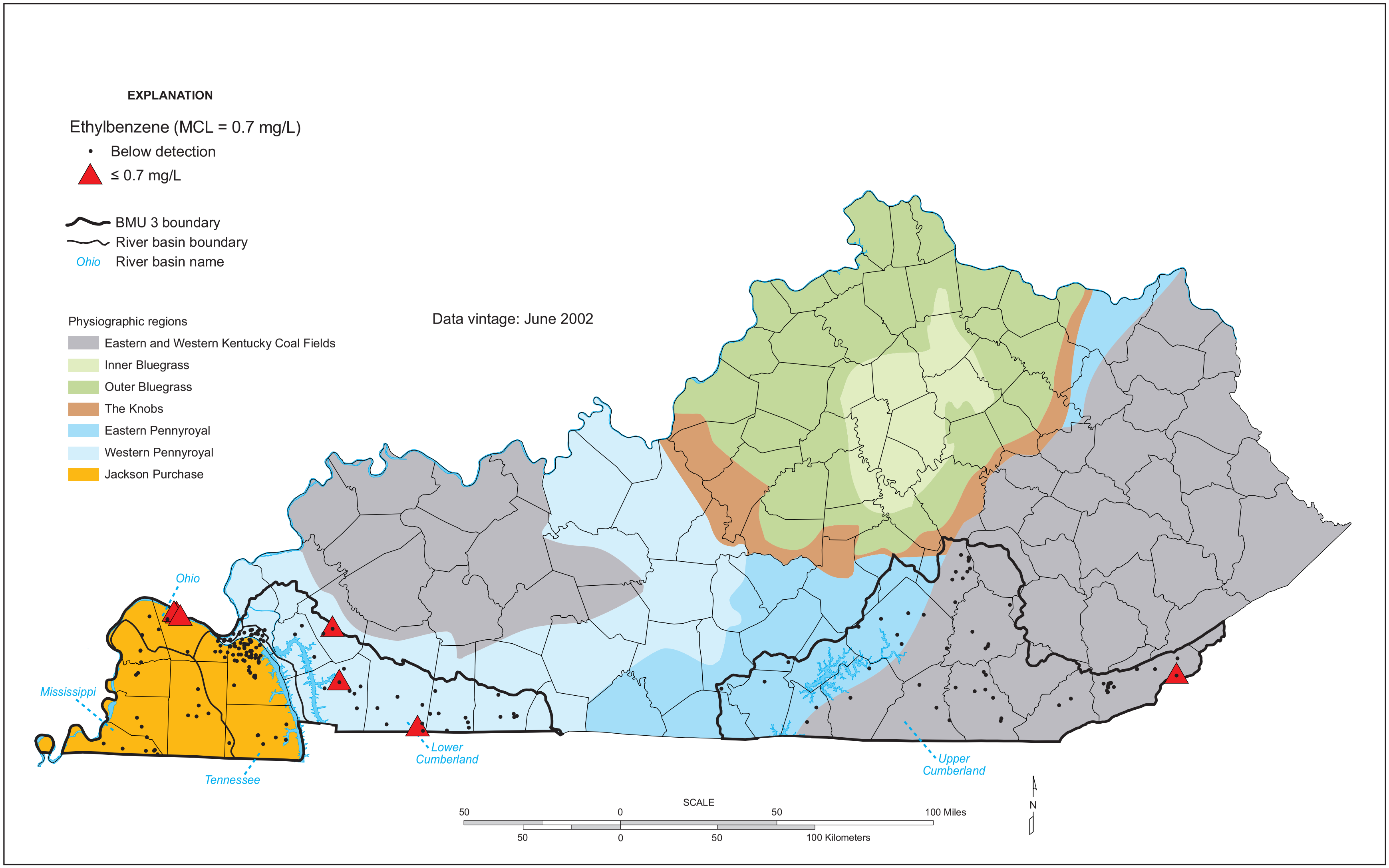

Figure 120. Sample sites and ranges of ethylbenzene values.

**Toluene.** Common sources of toluene in groundwater are discharge from petroleum refineries and leaking underground gasoline storage tanks. The potential health effects are damage to the nervous system, kidneys, or liver. The MCL for toluene is 1.0 mg/L.

The data repository contained 426 toluene measurements from 224 sites in the project area (Table 31). Fifteen of 426 measured concentrations in BMU 3 were above analytical detection limits; none exceeded the MCL. Toluene concentrations exceeded analytical detection limits at four springs and seven wells. Three of the springs where toluene was detected are in the Lower Cumberland River watershed of the Western Pennyroyal; one is in the Upper Cumberland River watershed of the  Eastern Kentucky Coal Field (Fig. 121). Four of the wells where toluene was detected are in the Ohio River watershed of the Jackson Purchase, two are in the Mississippi River watershed of the Jackson Purchase, and one is in the Upper Cumberland River watershed of the Eastern Kentucky Coal Field. Three of these wells are less than 60 ft deep, two are deeper than 140 ft, and two have no depth recorded.

**Table 31.** Summary of toluene values (mg/L).

| | |
|---|---|
| Measurements | 426 |
| Maximum | 0.0100 |
| 75th percentile | < 0.001 |
| Median | < 0.0005 |
| 25th percentile | < 0.0005 |
| Minimum | < 0.0005 |
| Interquartile range | na |
| Sites | 224 |
| MCL | 1.0 |
| Sites > 1.0 | 0 |

< means analytical result reported as less than the stated value

In summary, toluene (like the other volatile organic chemicals) has been detected in groundwater in the project area at a few sites. Toluene has entered the shallow groundwater system and probably the intermediate groundwater system, as evidenced by a detectable concentration in a 265-ft-deep well.

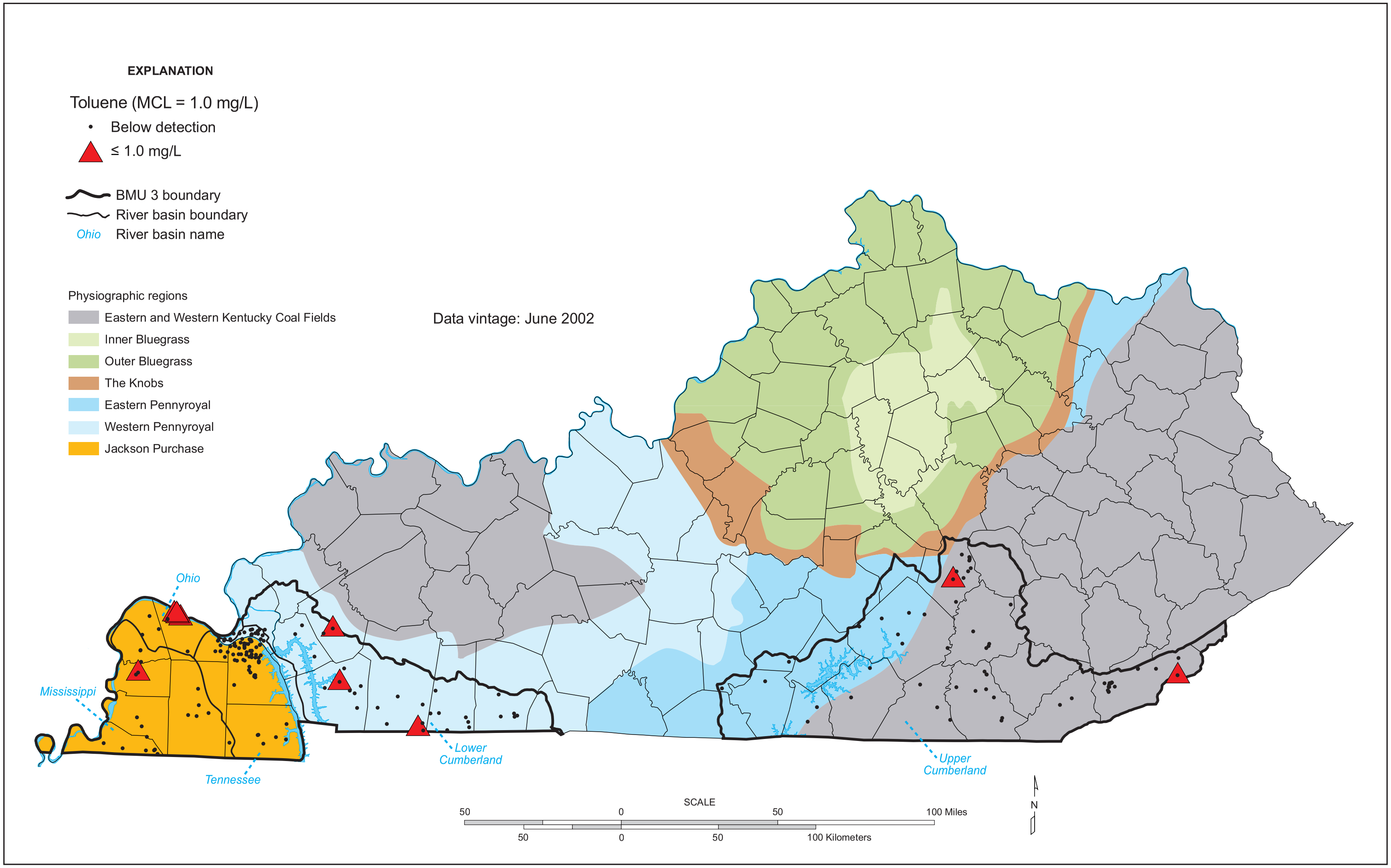

Figure 121. Sample sites and toluene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

**Xylenes (Total).** Xylenes in groundwater are usually the result of discharge from petroleum refineries or chemical factories, or leaking underground gasoline storage tanks. The primary health effect is damage to the nervous system. The MCL is 10 mg/L for the sum of O-xylene, P-xylene, and M-xylene.

The data repository contains 872 such measurements from 223 sites in BMU 3 (Table 32). Xylene analyses in the data repository are reported as "1,3-xylene and 1,4-xylene," "1,4-xylene," "M-xylene," "O-xylene," "P-xylene," "total xylene," "xylene," and "xylene mixed isomers." The variety of analyte names for xylene isomers in the data repository makes calculating total xylenes necessary at each site for a given sample collection.

Nineteen laboratory measurements for xylenes were above analytical detection limits; none were above the MCL. Nine sites had xylene concentrations greater than the analytical detection limit (Fig. 122). Of these, four are springs in the Lower Cumberland River watershed of the Western Pennyroyal, one is a spring in the Upper Cumberland River watershed of the Eastern Kentucky Coal Field, three are wells in the Ohio River watershed of the Jackson Purchase, and one is a well in the Upper Cumberland River watershed of the Eastern Kentucky Coal Field. Three of the wells have reported depths of less than 60 ft and one has no reported depth.

**Table 32.** Summary of xylene values (mg/L).

| | |
|---|---|
| Measurements | 872 |
| Maximum | < 0.5 |
| 75th percentile | < 0.001 |
| Median | < 0.0005 |
| 25th percentile | < 0.0005 |
| Minimum | 0.000275 |
| Interquartile range | na |
| Sites | 223 |
| MCL | 10.0 |
| Sites > 10.0 | 0 |

< means analytical result reported as less than the stated value

In summary, few sampled sites had total xylene concentrations that were above analytical detection limits. Springs and shallow wells are most likely to have detectable xylene levels, indicating that the shallow groundwater system has been affected in some areas.

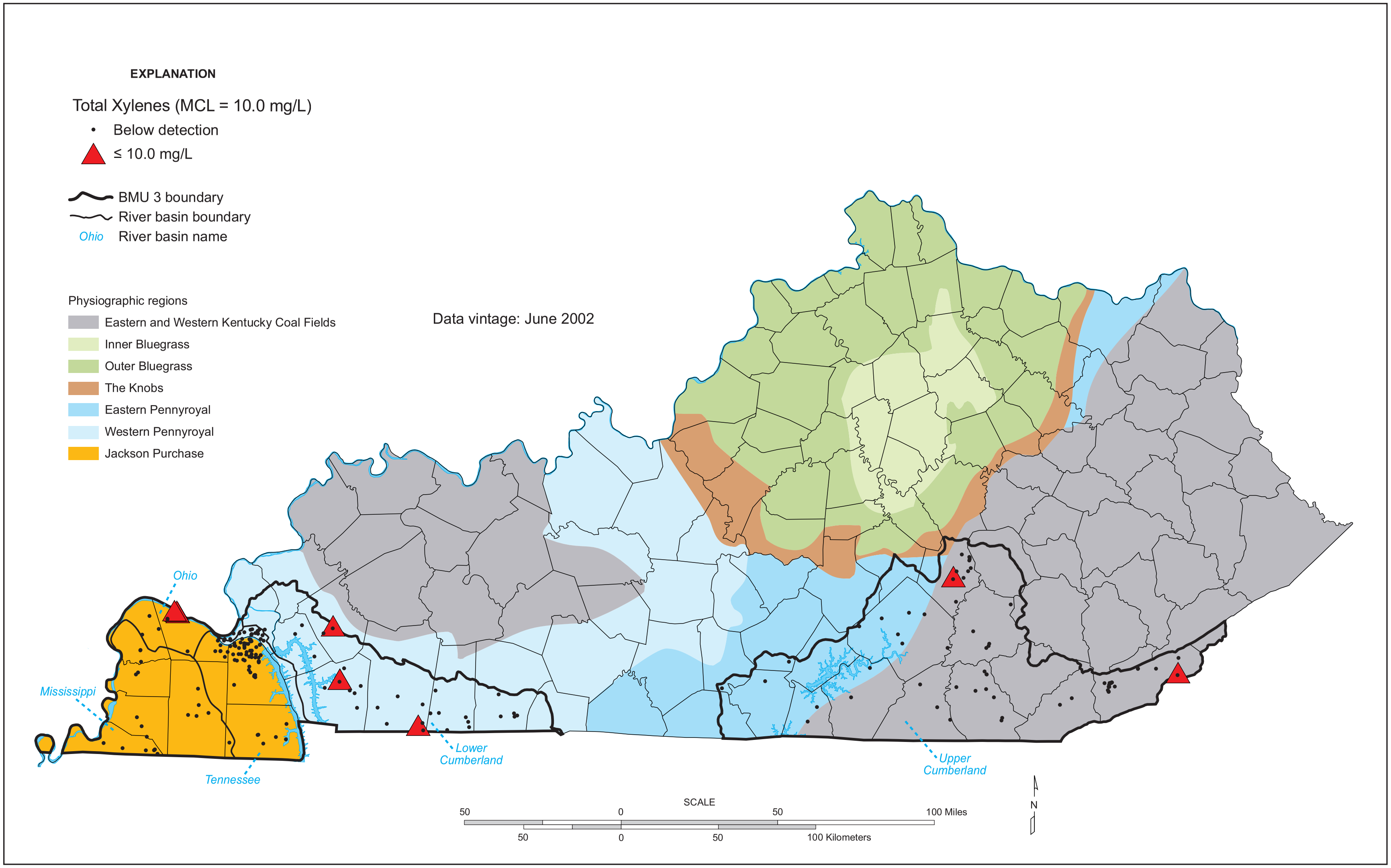

Figure 122. Sample sites and total xylene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

**MTBE (methyl tertiary-butyl ether).** MTBE is a gasoline additive used to promote combustion and reduce emissions. The primary sources of MTBE in groundwater are leaks from gasoline storage tanks or gasoline spills. Potential health effects have not been established; however, the Division of Water has set a risk-based water-quality standard of 0.050 mg/L.

The data repository contained 329 MTBE measurements at 106 sites in BMU 3 (Table 33). Seven of the reported values were greater than analytical detection limits; none exceeded the Division of Water–recommended level of 0.050 mg/L. MTBE exceeded the DEP recommended value at two springs and one well of unrecorded depth in the Lower Cumberland River watershed of the Western Pennyroyal, and one well of unrecorded depth in the Upper Cumberland River watershed of the Eastern Kentucky Coal Field (Fig. 123).

In summary, MTBE generally does not occur at detectable levels in water from wells and springs in the project area. Three of the four sites where MTBE was detected are springs or shallow wells in the carbonate, karst terrain of the Western Pennyroyal Region.

**Table 33.** Summary of MTBE values (mg/L).

| | |
|---|---|
| Measurements | 329 |
| Maximum | 0.00689 |
| 75th percentile | < 0.001 |
| Median | < 0.001 |
| 25th percentile | < 0.001 |
| Minimum | 0.00051 |
| Interquartile range | na |
| Sites | 106 |
| DOW recommended value | 0.05 |
| Sites > 0.05 | 0 |

< means analytical result reported as less than the stated value

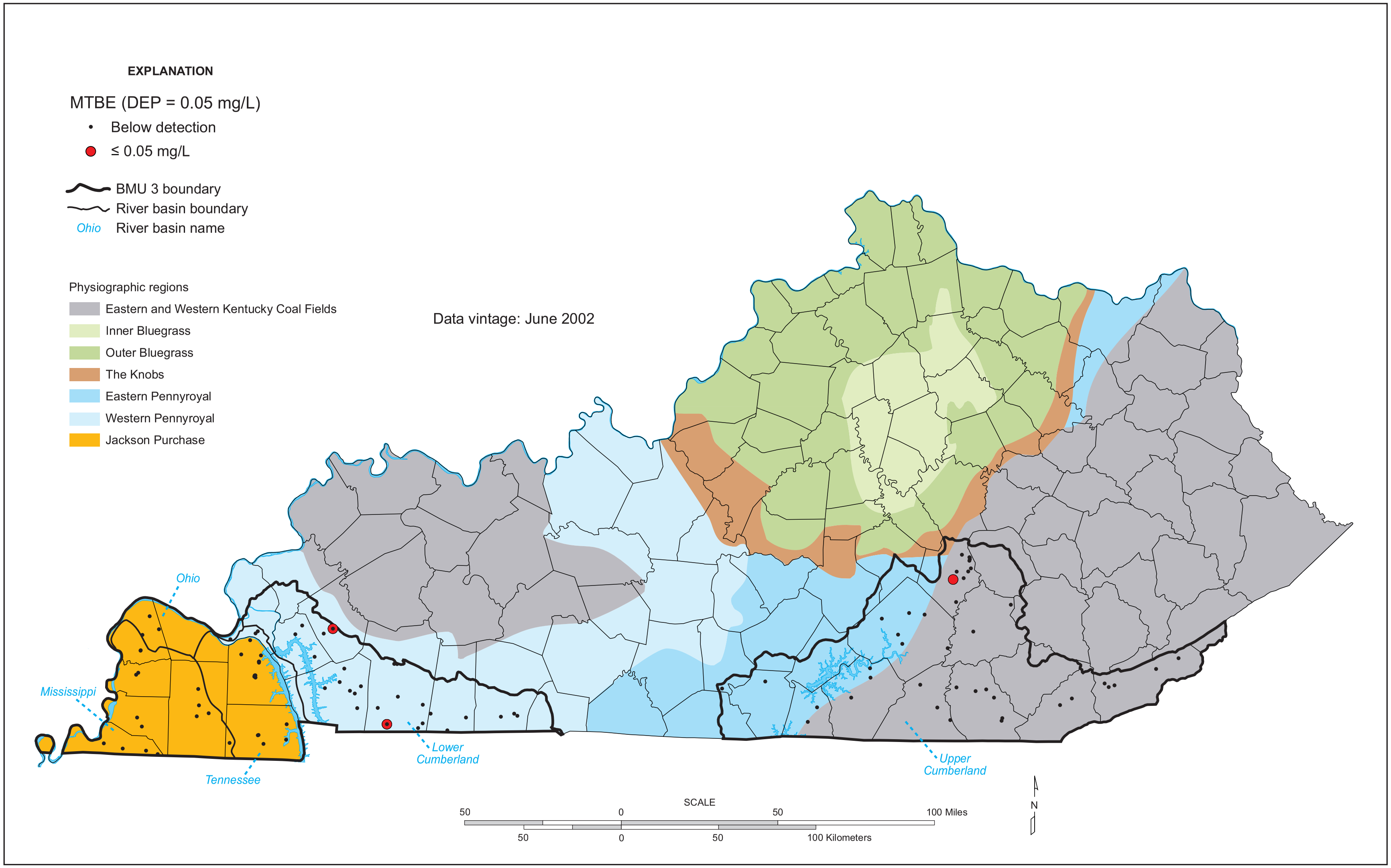

Figure 123. Sample sites and MTBE values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

# Summary and Conclusions

The goal of this project was to summarize and evaluate groundwater quality from Basin Management Unit 3 using results of analyses that were stored in the Kentucky Groundwater Data Repository. The results are important to resource planners, environmental quality regulators, researchers, and private citizens.

This report summarizes thousands of analytical results from thousands of wells and springs in BMU 3 (watersheds of the Upper and Lower Cumberland and Tennessee Rivers, and the Mississippi and Ohio Rivers in the Jackson Purchase) for important groundwater-quality parameters. Twenty-eight analytes, selected by the Kentucky Division of Water, are considered: basic groundwater parameters and major ions (conductance, hardness, total dissolved solids, total suspended solids, pH, chloride, sulfate, iron, and manganese); inorganic solutes that can affect human health (fluoride, arsenic, barium, and mercury); nutrients (ammonia, nitrate, nitrite, orthophosphate, and total phosphorus); pesticides (alachlor, atrazine, cyanazine, metolachlor, and simazine); and volatile organic compounds (benzene, ethylbenzene, toluene, xylenes, and MTBE). The number of measurements; number of sites; maximum, third quartile, median, first quartile, and minimum values; and number of sites at which maximum contaminant levels or other significant values are exceeded were tabulated for each analyte. Probability plots and box-and-whisker diagrams illustrate the data population, and the data are mapped to show sample site distribution.

Overall quality of Kentucky groundwater in BMU 3 is good. There are many wells and springs where groundwater exceeds recommended levels for water properties, inorganic anions, metals, nutrients, pesticides, and volatile organic chemicals, however. In some cases, the sources appear to be entirely natural; in other cases, there is clear evidence of contamination by nonpoint-source chemicals. Table 34 summarizes the findings.

General water properties (pH, total dissolved solids, total suspended solids, electrical conductance, and hardness) and inorganic ions and metals (chloride, sulfate, fluoride, arsenic, barium, mercury, iron, and manganese) are largely controlled by bedrock lithology. Some exceptionally high values of conductance, hardness, chloride, and sulfate may be the effects of deep brines associated with coal fields or oil and gas production, and some exceptionally low pH values may show the input of mine drainage.

Nutrient concentrations, particularly nitrate-nitrogen, show a strong contribution from agricultural practices. Springs and shallow wells generally have higher nutrient concentrations than wells that produce water from intermediate or deep strata.

Pesticides are synthetic organic chemicals that do not occur naturally. The presence of any detectable pesticide in groundwater indicates a nonpoint-source contribution from agricultural or suburban applications. The relative scarcity of detectable pesticide concentrations found in this study may be misleading, for two reasons. First, shallow wells in rural areas, those most susceptible to pesticide contamination, were not specific targets for sampling in the ambient groundwater-quality investigations that provide much of the data for this summary. Second, pesticide levels in groundwater are known to be highest following applications and after rainfalls. Sampling one time or on a quarterly schedule may miss the presence of pesticides if the sampling does not closely follow field and lawn applications or significant rainfalls. High pesticide concentrations in water from a well or spring are a health hazard when the water is used regularly for domestic purposes, even though the available analyses did not show high pesticide concentrations at the time of sample collection. For these reasons, pesticides are likely more common in wells and springs, and potentially a greater health threat than these data sets suggest.

Like pesticides, refined volatile organic chemicals generally do not occur naturally in groundwater and can have significant chronic health effects at very low concentrations. The occurrence of volatile organic chemicals in groundwater is not natural and can only be the result of human activities. This project was designed to exclude analyses of groundwater from wells or springs that were known to be affected by leaking underground storage tanks and other sources of volatile organic chemicals. Detection of volatile organic chemicals in wells and springs that were previously thought to be free of such compounds suggests that volatile organic chemicals are a greater threat to groundwater than was previously thought.

Throughout the project area, springs and shallow wells are more likely to have potentially harmful levels of metals, nutrients, pesticides, and volatile organic chemicals than intermediate or deep wells. The potential contamination of the shallow groundwater system (springs and shallow wells) is cause for concern, as is the need to protect the intermediate and deeper groundwater system.

**Table 34.** Summary of nonpoint-source effects on groundwater quality in Basin Management Unit 3.

| | Parameter | No Significant Impact on Groundwater Quality | Possible Impact on Groundwater Quality | Definite Impact on Groundwater Quality |
|---|---|---|---|---|
| **Water Properties** | Conductance | | X | |
| | Hardness | | X | |
| | pH | | X | |
| | Total dissolved solids | X | | |
| | Total suspended solids | X | | |
| **Inorganic Ions** | Chloride | | X | |
| | Sulfate | | X | |
| | Fluoride | X | | |
| **Metals** | Arsenic | X | | |
| | Barium | X | | |
| | Iron | X | | |
| | Manganese | X | | |
| | Mercury | X | | |
| **Nutrients** | Ammonia-nitrogen | | X | |
| | Nitrate-nitrogen | | | X |
| | Nitrite-nitrogen | X | | |
| | Orthophosphate-phosphorus | | X | |
| | Total phosphorus | | X | |
| **Water Properties** | 2,4-D | | | X |
| | Alachlor | | | X |
| | Atrazine | | | X |
| | Cyanazine | | | X |
| | Metolachlor | | | X |
| | Simazine | | | X |
| **Volatile Organic Compounds** | Benzene | | | X |
| | Ethylbenzene | | | X |
| | Toluene | | | X |
| | Xylenes | | | X |
| | MTBE | | | X |

# Acknowledgments

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# 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)

**Prepared by**
**R. Stephen Fisher, Geologist**
**Water Resources Section**
**Kentucky Geological Survey**
**University of Kentucky**
**and**
**Peter T. Goodmann, Manager, Groundwater Branch**
**Kentucky Division of Water**

## 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: ____________ ºC |
| 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<br>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)<br>**Alkalinity, Conductivity, pH, TSS, TDS**<br>(Methodds: 310.1, 120.1, 150.1, 160.2, 160.1, respectively) | | 1000 ml<br>Rigid Plastic | Filtered<br>$HNO_3$<br>Cool to 4ºC | **Dissolved Metals by ICP**<br>plus Arsenic, Lead, Mercury, Selenium<br>(Method 200.7) |
| | 1000 ml<br>Plastic | $H_2SO_4$<br>Cool to 4ºC | **$NH_3$/TKN/TOC/Total P**<br>(Methods: 350.1, 351.1, 415.1, 365.4, respectively; holding time 28 days) | | 1000 ml<br>Rigid Plastic | $HNO_3$<br>Cool to 4ºC | **Total Metals by ICP**<br>plus Arsenic, Lead, Mercury, Selenium<br>(Method 200.7) |
| | 3 - 4 ml VOA vial and field blank | HCl | **VOC's (report MTBE)**<br>(Method 8260; holding time 14 days) | | 1000 ml<br>Glass | Cool to 4ºC | **N/P Pesticides**<br>(Method 507; holding time 7 days) |
| | 1000 ml<br>Glass | Cool to 4ºC | **Herbicides**<br>(Method 515.1; holding time 7 days) | | 1000 ml<br>Glass | Cool to 4ºC | **Pesticides/PCBs**<br>(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)