Summary and Evaluation of Groundwater Quality in the Upper Cumberland, Lower Cumberland, Green, Tradewater, Tennessee, and Mississippi River Basins

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EXECUTIVE SUMMARY

The Kentucky Geological Survey (University of Kentucky) and the Kentucky Division of Water (Kentucky Natural Resources and Environmental Protection Cabinet) are evaluating groundwater quality throughout the Commonwealth to determine regional conditions, assess impacts of nonpoint-source pollutants, provide a baseline for detecting changes, and provide essential information for environmental protection and resource management. These evaluations are being conducted in stages to also provide information for the Kentucky Watershed Management Framework. This report summarizes results of analyses of groundwater samples from wells and springs in Kentucky basin management unit 3 (watersheds of the Upper and Lower Cumberland River, the Tennessee River, and tributaries of the Ohio River and Mississippi River in the Jackson Purchase Region) and 4 (watersheds of the Green River, the Tradewater River, and adjacent tributaries of the Ohio River).

Analytical results for selected water properties, major and minor inorganic ions, metals, nutrients, pesticides, and volatile organic chemicals were retrieved from the Kentucky Groundwater Data Repository. This 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. Summary 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 describe the data. Map views show well and spring locations and sites where water-quality standards were met or exceeded. Normal probability plots show data distributions in each basin management unit. Box-and-whisker diagrams compare values between physiographic regions, major watersheds, wells and springs, and other significant groupings. Plots of concentrations versus well depth are used to compare groundwater quality in shallow, intermediate, and deep flow systems.

Table E1 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 conductance, hardness, chloride, and sulfate may be affected by nearby 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) do not occur naturally in groundwater. Detection of these man-made chemicals in groundwater must be attributed to contamination.

Table E1. Summary of nonpoint-source effects on groundwater quality in BMU 3 and 4.

	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

INTRODUCTION

Purpose

Evaluating groundwater quality, its suitability for various uses, the sources of chemicals in groundwater, and the impacts of nonpoint-source contaminants is essential for making wise decisions concerning the use, management, and protection of this vital resource. The purpose of this report is to summarize and evaluate groundwater quality in basin management units (BMU) 3 and 4 using analytical results stored in the Kentucky Groundwater Data Repository, which is maintained by the Kentucky Geological Survey (KGS).

Goals

The goals of this report are to (1) determine the number of sampled sites and reliable groundwater-quality analyses in the study area, (2) summarize general water 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 (NPS) chemicals have entered the groundwater system, and (6) report 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 that are threatened by NPS chemicals, (3) identify areas where NPS chemicals have entered the groundwater system and future NPS investigations and implementation of best management practices (BMP's) are needed, (4) provide information for watershed assessment reports, (5) provide groundwater-quality data to the Kentucky Division of Water (DOW) Groundwater Protection program, (6) help the DOW Wellhead Protection program rank protection areas and activities, including the development, implementation, and evaluation of best management practices, and (7) provide critical information for long-term protection and management of water resources.

Background

Evaluating groundwater quality is particularly important in Kentucky, because groundwater use is extensive and will continue to be so. The 1990 census data and recent DOW estimates indicate that approximately 60 percent of public water-supply companies use groundwater as a sole or contributing water source, more than 25 percent of the population depends on groundwater for household use, and more than 226 million gallons of groundwater is consumed daily by individuals, municipalities, utilities, businesses, and farms. Groundwater will continue to be important to Kentuckians because economic and logistical factors make it expensive or impractical to replace groundwater with surface-water supplies, particularly in rural areas. It has been estimated that approximately 400,000 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 ambient groundwater quality; that is, regional groundwater quality that is not affected by point-source contamination. Both natural processes and anthropogenic 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 describe nonpoint-source contamination of regional groundwater systems in the study area. In the 1960's and early 1970's the U.S. Geological Survey (USGS) published reconnaissance studies of the geology, groundwater supplies, and general groundwater quality in Kentucky. These reports include a Hydrologic Atlas for each 15-minute quadrangle in the state (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 Coal Field (Price and others, 1962), Western Coal Field

(Maxwell and Devaul, 1962), and Mississippian Plateau Region, herein referred to as the Eastern and Western Pennyroyal Regions (Brown and Lambert, 1963) in this study area. 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), the Scottsville area of the Western Pennyroyal Region (Hopkins, 1963), the Tradewater River Basin of the Western Coal Field (Grubb and Ryder, 1972), the Henderson area of the Western Coal Field (Harvey, 1956), and the Hopkinsville quadrangle of the Western Coal Field (Walker, 1956). 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). None of these reports addressed regional groundwater quality or the effects of nonpoint-source contaminants on groundwater. 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, Kentucky (Western Pennyroyal Region).

As of January 2000, DOW sampled approximately 150 wells and springs in the 20,970-square-mile area; approximately two-thirds of these sites were sampled quarterly as part of the ambient groundwater monitoring program. The results were used for programmatic purposes and stored in the DOW groundwater database, but were not widely available in an interpreted form.

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 KGS and other State, Federal, and local agencies. The National Uranium Resource Evaluation (NURE) program provided a second large source of analyses of groundwater, surface water, and stream sediments (Smith, 2001). Digital records from both these reports are stored in the Kentucky Groundwater Data Repository, and were used in this report.

PROJECT AREA

The project area is composed of the watersheds of the Upper Cumberland, Lower Cumberland, Tennessee, Tradewater, and Green Rivers; tributaries of the Mississippi River in the Jackson Purchase Region; and tributaries of the Ohio River adjacent to these major watersheds in southwestern and western Kentucky (Fig. 1). This region was chosen for three reasons. First, it was recognized that the available resources did not permit an evaluation of groundwater quality for the entire state; a smaller area must be chosen. Second, the Kentucky Division of Water Watershed Management Framework uses major river basins as the basis for coordinating watershed investigations and program implementation (Kentucky Division of Water, 1997). The Division of Water's Watershed Management Framework groups Kentucky's 12 major river basins into five basin management units (Fig. 1). Conducting an evaluation of existing groundwater data for wells and springs in the project area would provide groundwater information at the same time that surface-water quality data were being gathered in BMU's 3 and 4. Third, a complementary project had been proposed to evaluate groundwater data in the remainder of the state (BMU's 1, 2, and 5). That project was subsequently approved and is in progress.

The project area includes six of Kentucky's eight physiographic regions (Fig. 1), each distinguished by unique geology, topography, and soil types (McDowell, 1986; Newell, 1986). This physiographic framework is very important 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.

Basin Management Unit 3

Basin management unit 3 (watersheds of the Upper and Lower Cumberland and Tennessee Rivers, the Jackson Purchase Region, and adjacent Ohio River tributaries) includes the mountainous terrain of the Eastern Kentucky Coal Field, the karst landscape of the Eastern and Western Pennyroyal Regions, and the largely agricultural Jackson Purchase (Fig. 1). The Upper Cumberland River has headwaters in the Eastern Kentucky Coal Field. This region is characterized by 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. Steep hillsides separate narrow, flat river valleys from sharp, sinuous

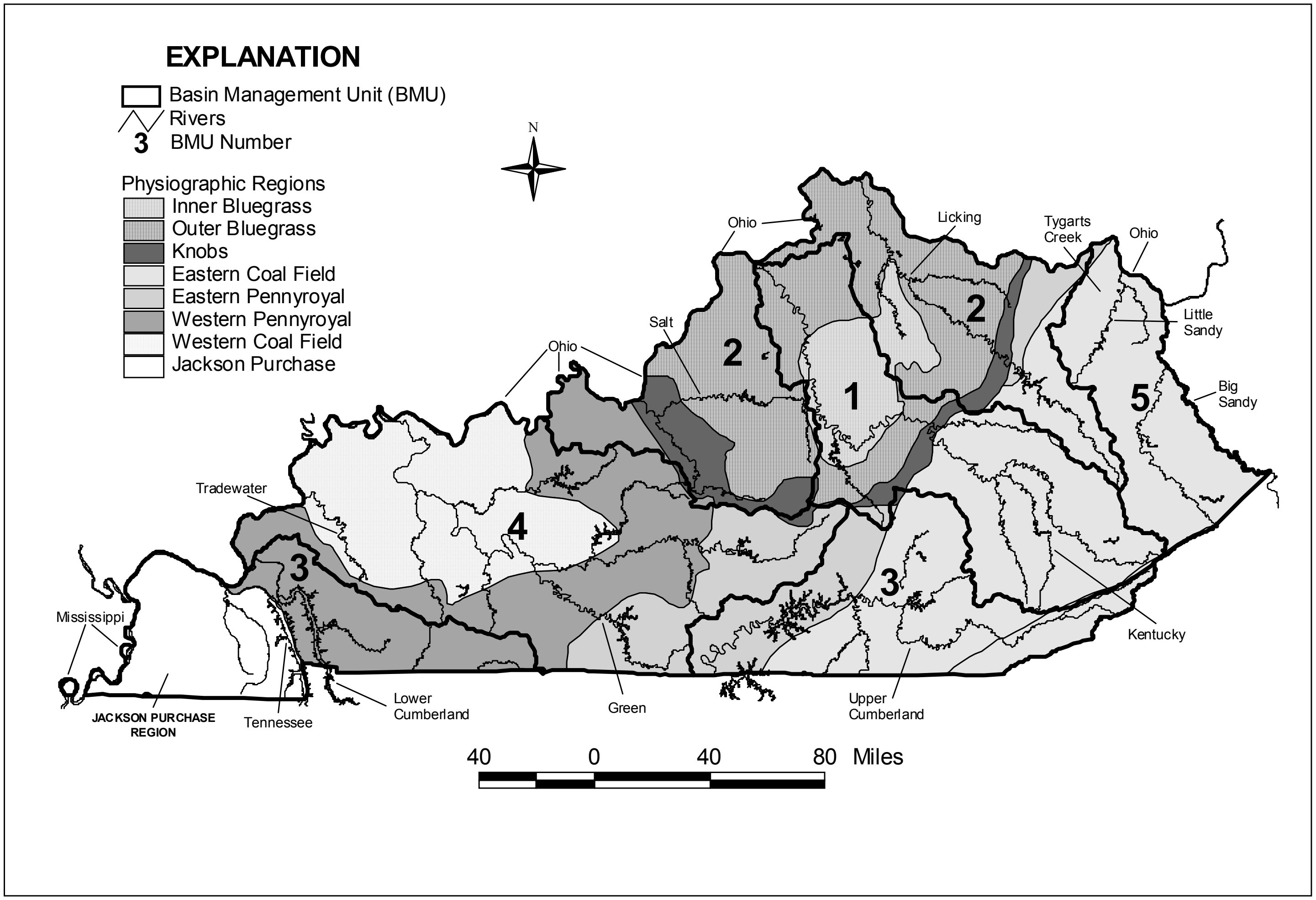


Figure 1. Major rivers, physiographic regions, and basin management units.

mountain crests (Newell, 1986). Downstream from the Eastern Kentucky Coal Field, the Cumberland River enters the Eastern Pennyroyal Region of Kentucky, dips into northern Tennessee, and re-enters Kentucky in the Western Pennyroyal Region. The Pennyroyal Plateau consists 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 western part of BMU 3 contains the watersheds of the Tennessee River and tributaries to the Ohio and Mississippi Rivers in the Jackson Purchase. The region is underlain by unconsolidated to poorly consolidated gravel, sand, silt, and clayey sediments (Newell, 1986).

Land uses and nonpoint-source chemical threats to groundwater quality in BMU 3 include oil and gas production; active and abandoned coal mines; leaking sewage disposal systems; deforested areas in the Eastern Kentucky Coal Field, and farmland, 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 the following counties: Adair, Ballard, Bell, Caldwell, Calloway, Carlisle, Casey, Christian, Clinton, Crittenden, Cumberland, Fulton, Graves, Harlan, Hickman, Jackson, Knox, Laurel, Lincoln, Livingston, Logan, Lyon, Marshall, McCracken, McCreary, Metcalfe, Monroe, Moore, Pulaski, Rockcastle, Russell, Simpson, Todd, Trigg, Wayne, and Whitley.

Basin Management Unit 4

Basin management unit 4 consists of the Green and Tradewater River watersheds. The Green River has headwaters in the carbonate Eastern Pennyroyal Region of south-central Kentucky and flows northwest toward the Ohio River. The Upper Green River flows over gently rolling karst terrain characterized by nearly horizontal limestones, sandstones, and shales. Sinkhole plains in this region collect precipitation and direct it to underground caves and solution channels. Discharge is ultimately to springs or streams. The world-famous Mammoth Cave is located in the karst section of the Green River drainage. A small part of the Green River headwater region is in The Knobs physiographic region, a narrow belt of isolated hills composed of sandstone and shale. The Green River flows through the Western Kentucky Coal Field, which is characterized by nearly horizontal loess, sandstone, shale, and coal beds. Groundwater flow in the coal field is mainly through near-surface fractures, with discharge to local streams. The Tradewater River flows northwestward from its source in the carbonate Western Pennyroyal Region to the Ohio

River. It first crosses karst terrain similar to that of the Eastern Pennyroyal Region, then enters a gently rolling region underlain by unconsolidated sand and silt. Groundwater flow in the unconsolidated subsurface is predominantly porous-media flow, distinctly different from the karstic or fracture flow systems elsewhere in the region.

Land uses and NPS threats in BMU 4 are varied. Agricultural land accounts for approximately 55 percent of the region, forest land accounts for approximately 39 percent, and residential land and mined lands in the Western Kentucky Coal Field account for the remainder (Kentucky Division of Water, 2001). The major NPS threats are fertilizers, pesticides, animal wastes, mine drainage, runoff from mine spoil, leaking septic systems, and urban stormwater runoff.

BMU 4 includes the following counties: Adair, Allen, Barren, Breckinridge, Butler, Caldwell, Casey, Christian, Crittenden, Cumberland, Daviess, Edmonson, Grayson, Green, Hancock, Hardin, Hart, Henderson, Hopkins, Larue, Lee, Lincoln, Livingston, Logan, McLean, Meade, Metcalfe, Monroe, Muhlenberg, Ohio, Perry, Pike, Pulaski, Rockcastle, Russell, Simpson, Taylor, Todd, Union, Warren, and Webster.

Hydrogeologic Unit Codes

The U.S. Geological Survey (USGS) has assigned watersheds hydrologic unit codes (HUC's) to identify regions, subregions, accounting units, and cataloging units (USGS, 1976). The HUC designations of watersheds in BMU's 3 and 4 are listed in Tables 1 and 2.

Table 1. Watershed names and 6-digit HUC designations for basin management units 3 and 4.

HUC 6	HUC 6 Name	BMU
051301	Upper Cumberland River	3
051302	Lower Cumberland River	3
060400	Lower Tennessee River	3
080101	Areas along the Mississippi River	3
080102	Mayfield and Obion Creeks, Bayou de Chien, Mississippi River in the Jackson Purchase Region	3
051100	Green River	4
051402	Tradewater River, Ohio River	4

Table 2. Watershed names and 8-digit HUC designations for basin management units 3 and 4.

HUC 8	HUC 8 Name	BMU
05130101	Upper Cumberland River	3
05130102	Rockcastle River	3
05130103	Cumberland River	3
05130104	South Fork Cumberland River	3
05130105	Dale Hollow Lake	3
05130205	Barkley Lake—Cumberland River	3
05130206	Lower Cumberland River—Red River	3
06040005	Tennessee River—Kentucky Lake	3
06040006	Clarks River	3
08010101	Mississippi River	3
08010201	Mayfield Creek, Obion Creek, Bayou de Chien	3
08010202	Mississippi River—Reelfoot Lake	3
05110001	Upper Green River	4
05110002	Barren River	4
05110003	Mud River—Green River	4
05110004	Rough River	4
05110005	Lower Green River	4
05110006	Pond River	4
05140201	Ohio River—Blackford Creek	4
05140202	Ohio River—Highland Creek	4
05140203	Ohio River—Deer Creek	4
05140205	Tradewater River	4
05140206	Ohio River—Massac Creek	3

Groundwater Sensitivity Regions

The potential for groundwater contamination is not uniform throughout the study. The vulnerability of groundwater to nonpoint-source contamination varies geographically across Kentucky, and vertically at any given location, in response to both natural and anthropogenic 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 anthropogenic 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). Briefly, 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 and Western Coal Fields, 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. However, two factors limit the usefulness of well depth as an indicator of groundwater system. 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 tap a deep groundwater flow system if the well is located near the discharge region of the groundwater flow system.

METHODS

Records for groundwater analyses from wells and springs in BMU's 3 and 4 were 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 are 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. Those activities are 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 parameters 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 NPS contaminants on groundwater. The parameters selected are:

General water properties: pH, total dissolved solids, conductance, hardness, 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 Groundwater Data Repository as of June 2002.

Both dissolved concentrations (measured on a sample that had been filtered to remove suspended particulate material) and total concentrations (measured on 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 (RCRA) 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 6-digit HUC number, major watershed name, and physiographic region designation so that the data from BMU's 3 and 4 could be grouped into these smaller categories. GIS coverages of 6-digit HUC's and physiographic regions were obtained from the KGS Web site (www.uky.edu/KGS/gis/intro.html).

2. Delete records that do not provide useful information.

The U.S. Environmental Protection Agency (EPA) has established maximum contaminant levels (MCL's) for chemicals that present health risks. Some analytical results in the Groundwater Data Repository were reported only as "less than" a detection limit, where the detection limit was greater than the MCL. 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 (e.g., see Helsel and Hirsch, 1992).

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 (IQR: 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 RCRA investigations (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 and percent of sites at which measurements exceeded water-quality standards.

Water-quality standards were provided by DOW (Table 3). Because there may have been many samples 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.

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

	Parameter	***Standard (mg/L unless otherwise noted)***	***Source***
Water Properties	Conductance	10,000 microsiemens	No MCL or SMCL, approximately corresponds to brackish water
	Hardness (calcium and magnesium)	Soft: 0 to 17 Slightly hard: 18 to 60 Moderately hard: 61 to 120 Hard: 121 to 180 Very hard: > 180	U.S. Geological Survey
	pH	6.5 to 8.5 pH units	SMCL
	Total dissolved solids	500	SMCL
	Total suspended solids	35	KPDES
Inorganic Ions	Chloride	250	SMCL
	Sulfate	250	SMCL
	Fluoride	4.0	MCL
Metals	Arsenic	0.010	MCL
	Barium	2.0	MCL
	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	0.07	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 (U.S. Environmental Protection Agency). Concentrations higher than the MCL may present health risks.

SMCL: Secondary maximum contaminant level (U.S. Environmental Protection Agency). Concentrations greater than the SMCL 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.

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 do 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 and percent of sites where concentrations exceed MCL's or other standard values for each BMU.

Normal probability plots (cumulative data plots) show the distribution of values as a percent of 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 mean 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 v. 4.1.

The general approach for each analyte is:

1. Define the analyte, summarize common natural sources, list relevant water-quality criteria, and describe how excessive amounts impact water use and human health.
2. Summarize analytical reports from BMU 3 and BMU 4 by constructing summary data tables and cumulative data plots.
3. Summarize data for each major watershed (6-digit HUC) by constructing box and whisker plots.
4. Show sample site distribution and sites where water-quality standards are met or exceeded by mapping sample sites and concentration ranges.
5. Summarize data for each physiographic region by constructing box and whisker plots.
6. Evaluate the impact on shallow (< 200 ft), intermediate (200 to 500 ft), and deep (> 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. For analytes where no significant differences were discerned for a particular comparison, that comparison is not presented.
7. Perform further analyses as indicated by patterns in mapped concentration ranges or by the nature of the analyte. The most common of these analyses is a comparison of dissolved versus total concentrations. For analytes where no significant differences were discerned for a particular comparison, that comparison is not presented.
8. Summarize potential causes of observed concentrations and distribution of values.

RESULTS

Water Properties

pH

The parameter 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 areas or sample sites. For these reasons it is one of the most important parameters that describe groundwater quality.

The pH of neutral (neither acidic or 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 value 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 bedrock can be even lower. In the absence of coal and associated 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 8.4.

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 (EPA) has established a secondary standard (SMCL) for pH of 6.5 to 8.5. Water with pH higher than 8.5 or lower than 6.5 can produce aesthetic effects such as staining and etching or scaling of equipment.

The data repository contained 2,550 pH values from 434 sites in BMU 3 and 1,009 pH values from 248 sites in BMU 4 (Table 4). The data summary shows differences in pH data between BMU's 3 and 4. The median pH value is greater in BMU 4 than in BMU 3, and the interquartile range is much smaller in BMU 4 (Table 4). Relatively few sites in either BMU had pH values greater than 8.5. However, sites having pH values less than 6.5 are common in BMU 3.

Table 4. Summary of pH measurements (standard pH units).

	BMU 3	BMU 4
Number of measurements	2,550	1,009
Number of sites	434	248
Maximum	9.5	12.4
3rd quartile	7.4	7.7
Median	6.9	7.5
1st quartile	6.3	7.4
Minimum	1.7	0.0
Interquartile range	6.3 to 7.4	7.4 to 7.7
Nr sites > 8.5	9	18
% sites > 8.5	2.1	7.2
Nr sites < 6.5	189	22
% sites < 6.5	43.5	12.9

SMCL: 6.5 to 8.5

These differences in pH values are illustrated in Figures 2 and 3. Measurements from BMU 3 follow a normal distribution between pH values of about 5.5 and 9, whereas values from BMU 4 follow a normal distribution only between pH values of about 7 to 8. Measured pH values in BMU 4 show high and low values that depart from the main trend of data, whereas values from BMU 3 tend to follow the same general distribution.

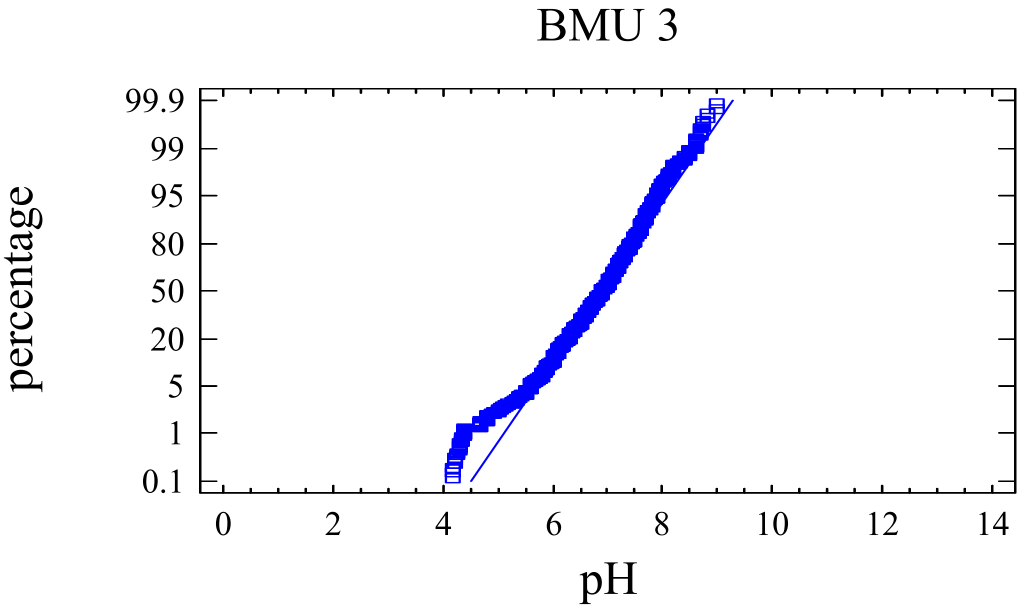


Figure 2. Cumulative plot of pH values from BMU 3. SMCL: 6.5 to 8.5.

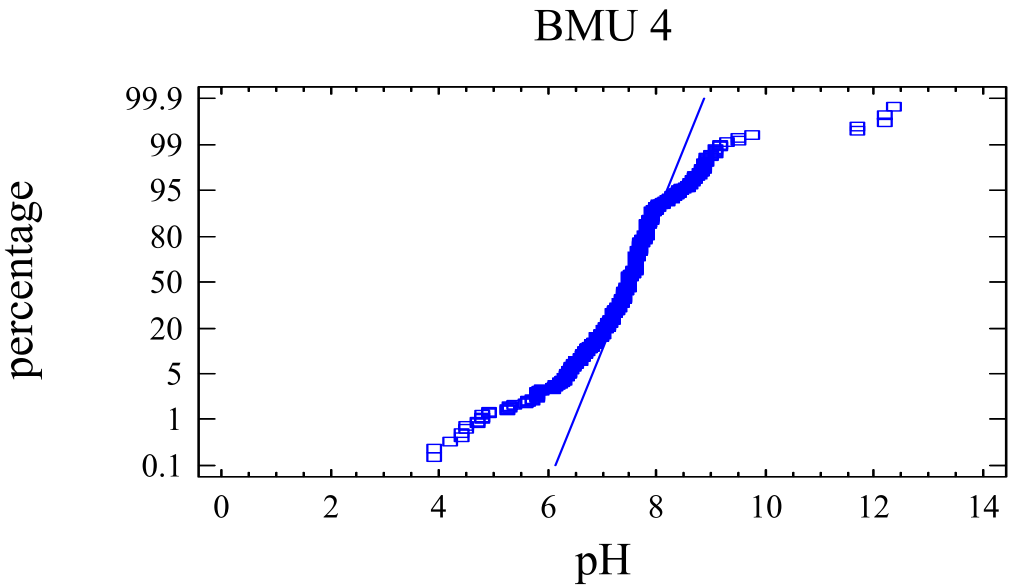


Figure 3. Cumulative plot of pH values from BMU 4. SMCL: 6.5 to 8.5.

Grouping pH values by major river basin (6-digit HUC; Fig. 4) shows that the highest values are in the Green River watershed and the lowest values are in the Upper Cumberland watershed. These two major river basins also have the greatest spread of pH data. The smallest total range of pH values is observed in the Lower Cumberland and Mississippi River watersheds. Samples from the Lower Cumberland, Mississippi, and Green River watersheds have relatively small interquartile ranges; that is, the central 50 percent of pH measurements are within one pH unit of each other.

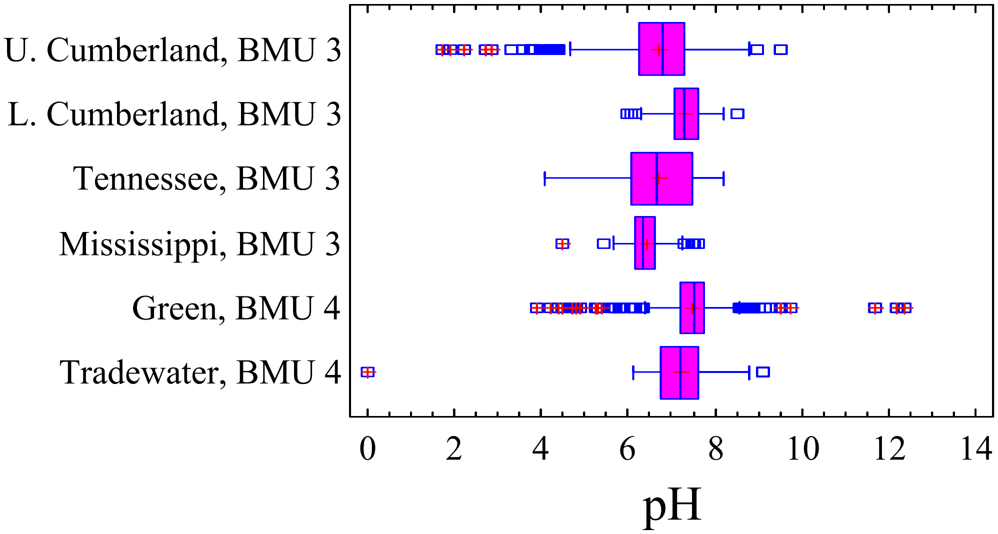


Figure 4. Summary of pH data grouped by major watershed (6-digit HUC) and BMU. SMCL: 6.5 to 8.5

The map (Fig. 5) shows that physiographic regions, and the underlying geology, strongly influence pH values. Values of pH range from less than 6.5 to greater than 8.5 in the geologically heterogeneous Eastern and Western Coal Fields, generally near neutral in the carbonate terrain of the Eastern and Western Pennyroyal Regions, and are generally less than 6.5 in the sandy Jackson Purchase Region.

A summary of pH values grouped by physiographic region (Fig. 6) confirms that different regions have different ranges of pH values. The large variability of pH values from sites in the Upper Cumberland Basin (Fig. 4) is due to variability in the Eastern Coal Field, not in the Eastern Pennyroyal, which is also in the Upper Cumberland watershed (Figs. 5 and 6). Similarly, the variability of pH values in the Green River watershed (Fig. 4) is caused by variability in the Western Coal Field, not in the Western Pennyroyal (Figs. 5 and 6). The low variability in the Lower Cumberland watershed and Jackson Purchase (Fig. 4) is a result of the physiographic and geologic uniformity within these watersheds (Figs. 5 and 6).

No comparison of total and dissolved pH is possible because pH is measured on unfiltered groundwater at the sample site. The range of pH values of wells and springs is similar. However, the scatter of pH values decreases, and pH trends toward higher values with well depth (Fig. 7).

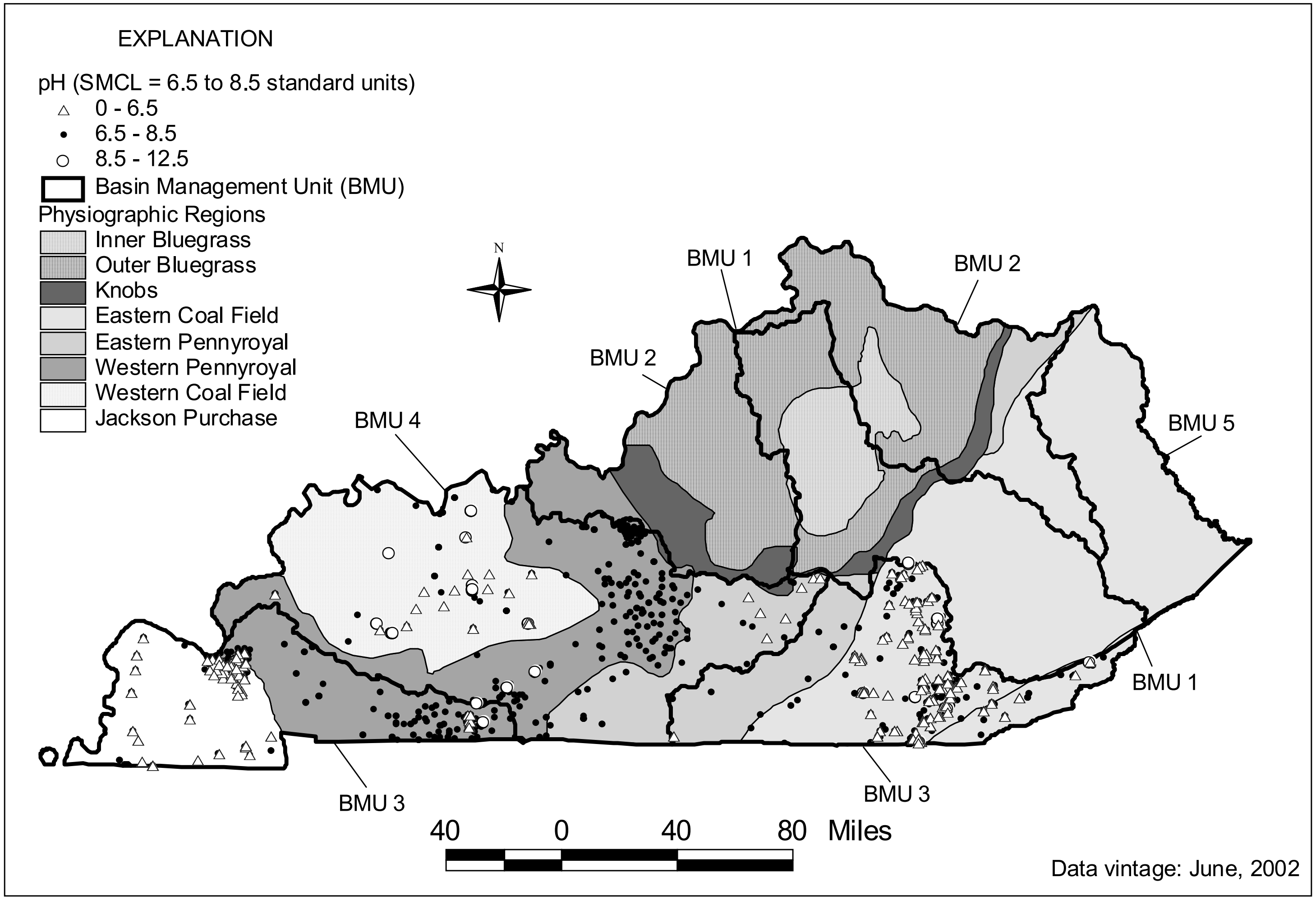


Figure 5. Sampled sites and ranges of pH measurements. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

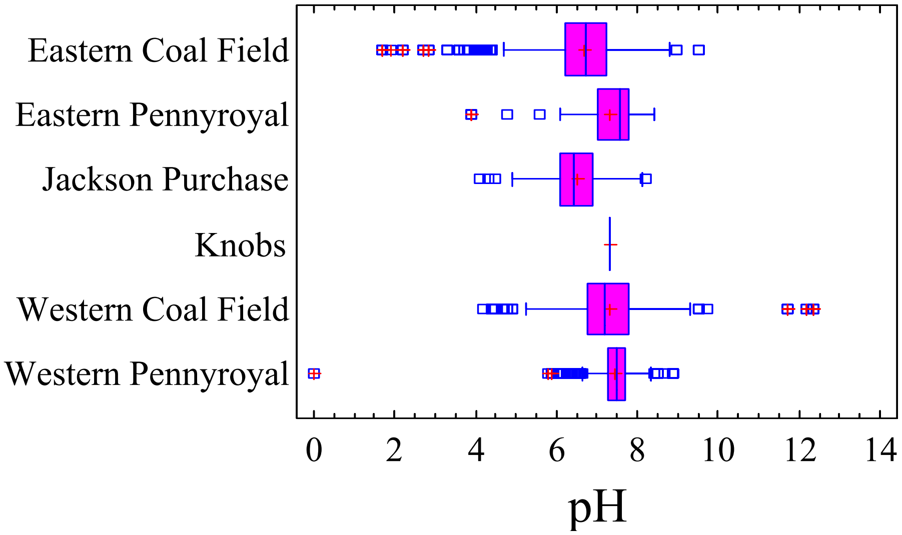


Figure 6. Summary of pH values grouped by physiographic region. SMCL: 6.5 to 8.5.

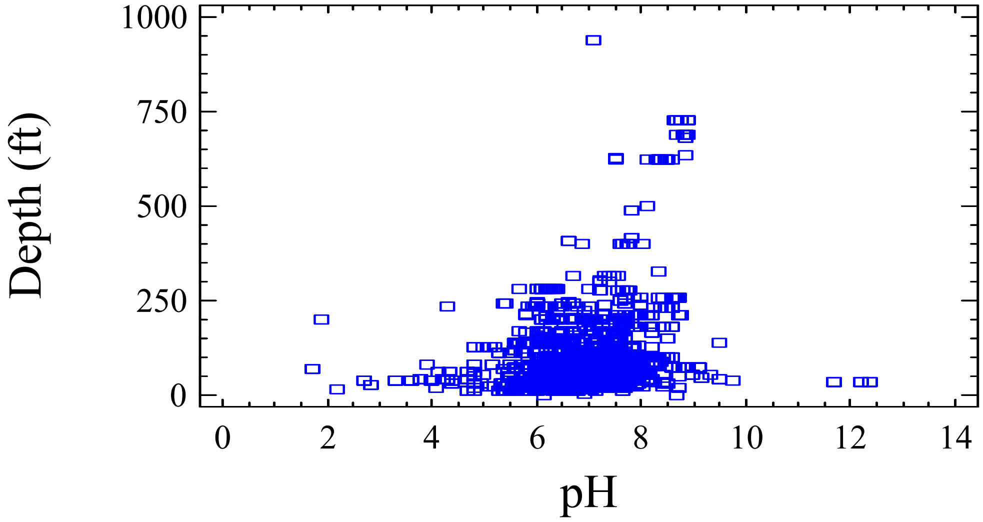


Figure 7. Plot of pH values versus well depth.

Summary: Sample site distribution is not uniform throughout the project area. The Eastern and Western Coal Fields are relatively well sampled, whereas large parts of the Eastern and Western Pennyroyal Regions have not been sampled. There are many sample sites in the Jackson Purchase Region; however, many of the sites are concentrated in a small area.

Groundwater pH values and ranges of values are most closely related to physiographic region, rather than to BMU or 6- or 8-digit HUC. Groundwater in the predominantly carbonate Eastern and Western Pennyroyal Regions is nearly neutral and shows relatively little scatter. In the

Eastern and Western Coal Fields, where bedrock lithology is more heterogeneous, groundwater pH is near neutral to slightly acidic, and shows a much wider range of values. Groundwater in the sandy Jackson Purchase is slightly acidic, probably because carbonate minerals are scarce there.

The minimum value (0.0) reported in the Western Pennyroyal Region is probably an error, but that cannot be confirmed from the database records. Values greater than 11.0 in the Western Coal Field and less than about 5.0 in the Jackson Purchase and the Eastern Pennyroyal Region may be the result of NPS contamination. In general, however, pH values seem to reflect bedrock geology rather than NPS effects. The pH of springs and shallow wells is much more variable than the pH observed in 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 is available (Fisher, 2002b) and can be viewed on the KGS Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

Total Dissolved Solids

Total dissolved solids (TDS) is the sum of all dissolved chemicals in water, expressed as mg/L. TDS can be calculated by adding all the solute concentrations from a full chemical analysis or measured as the weight of the residue remaining after a volume of water has been evaporated to dryness. TDS typically increases with sample depth or the distance that groundwater has traveled from recharge area to sample site. 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 U.S. EPA has set a secondary drinking water standard (SMCL) of 500 mg/L total dissolved solids. Water having TDS values greater than 500 mg/L has an unpleasant taste and may stain objects or precipitate scale.

The KGS data repository contained 632 reports of TDS at 150 sites in BMU 3 and 739 reports of TDS at 100 sites in BMU 4. Total dissolved solids measurements are summarized in terms of suitability for various uses (Table 5). Nearly all samples and sites yielded potable water. Three measurements in BMU 3 exceeded 2,500 mg/L; no measurements exceeded 5,000 mg/L. Two measurements in BMU 4 exceeded 2,500 mg/L and one measurement exceeded 5,000 mg/L.

Cumulative data plots (Figs. 8 and 9) show that the data distribution is different in the two BMU's and that there are more total dissolved solids values greater than 500 mg/L in BMU 3 than in BMU 4. A summary plot of the data grouped by major watershed (Fig. 10) shows the highest values occur in the Lower Cumberland and Green River watersheds, whereas sites in the Tennessee River watershed have the least variability.

The map (Fig. 11) shows that potable water is present throughout the area, and that there are few wells or springs where saline, brackish, or brine water was encountered. Groundwater in the Eastern Pennyroyal has the smallest range of values, whereas samples from the Western Coal Field and Western Pennyroyal have the greatest variability of TDS values (Fig. 12).

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

Total Dissolved Solids (mg/L)	**Percent of analyses**	**Percent of sites**
Basin management unit 3		
Potable water (0 to 500)	94	87
Slightly saline (501 to 1,000)	3	7
Medium saline (1,001 to 2,500)	3	5
Saline (2,501 to 5,000)	< 1	< 1
Brackish (5,001 to 35,000)	0	0
Brine (> 35,000)	0	0
Basin management unit 4		
potable water (0 to 500)	98	89
slightly saline (501 to 1,000)	2	9
medium saline (1,001 to 2,500)	0	0
saline (2,501 to 5,000)	< 1	2
brackish (5,001 to 35,000)	< 1	< 1
brine (> 35,000)	0	0

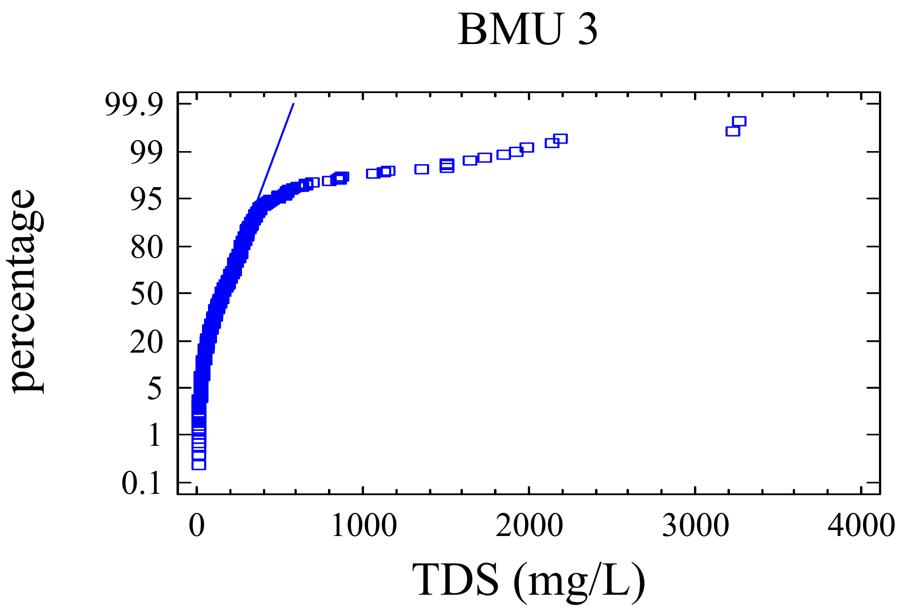


Figure 8. Cumulative plot of TDS values from sites in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. SMCL = 500 mg/L.

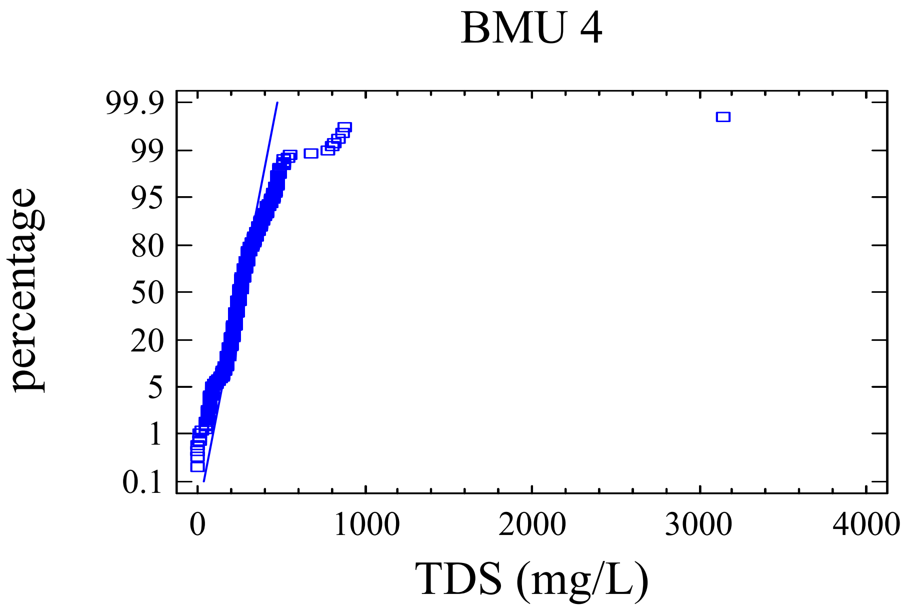


Figure 9. Cumulative plot of TDS values from sites in BMU 4. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. SMCL = 500 mg/L.

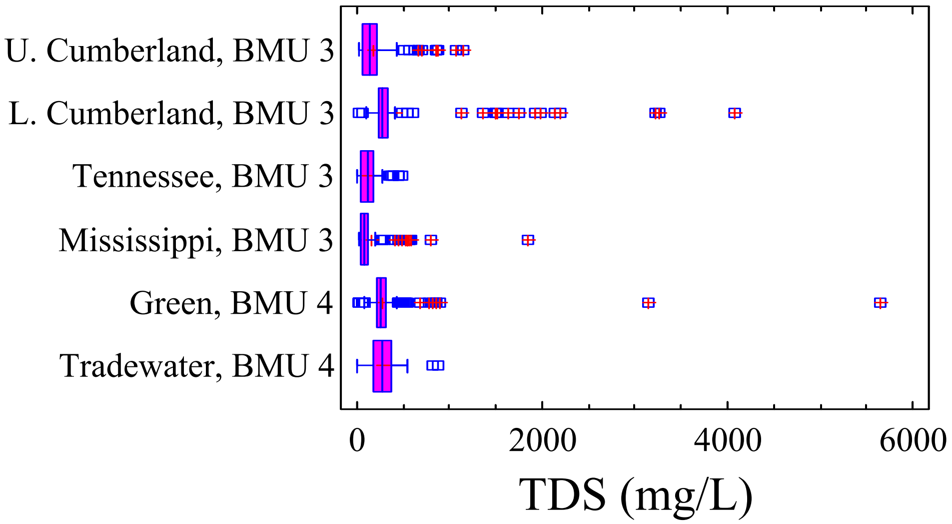


Figure 10. Summary plot of total dissolved solids values grouped by major watershed. SMCL = 500 mg/L.

Springs and wells have approximately the same median TDS value and a similar interquartile range (Fig. 13). However, the highest TDS values are found in water wells (Fig. 13). There is no systematic trend of TDS values with well depth; however, the highest TDS values occur in wells shallower than about 200 ft. (Fig. 14).

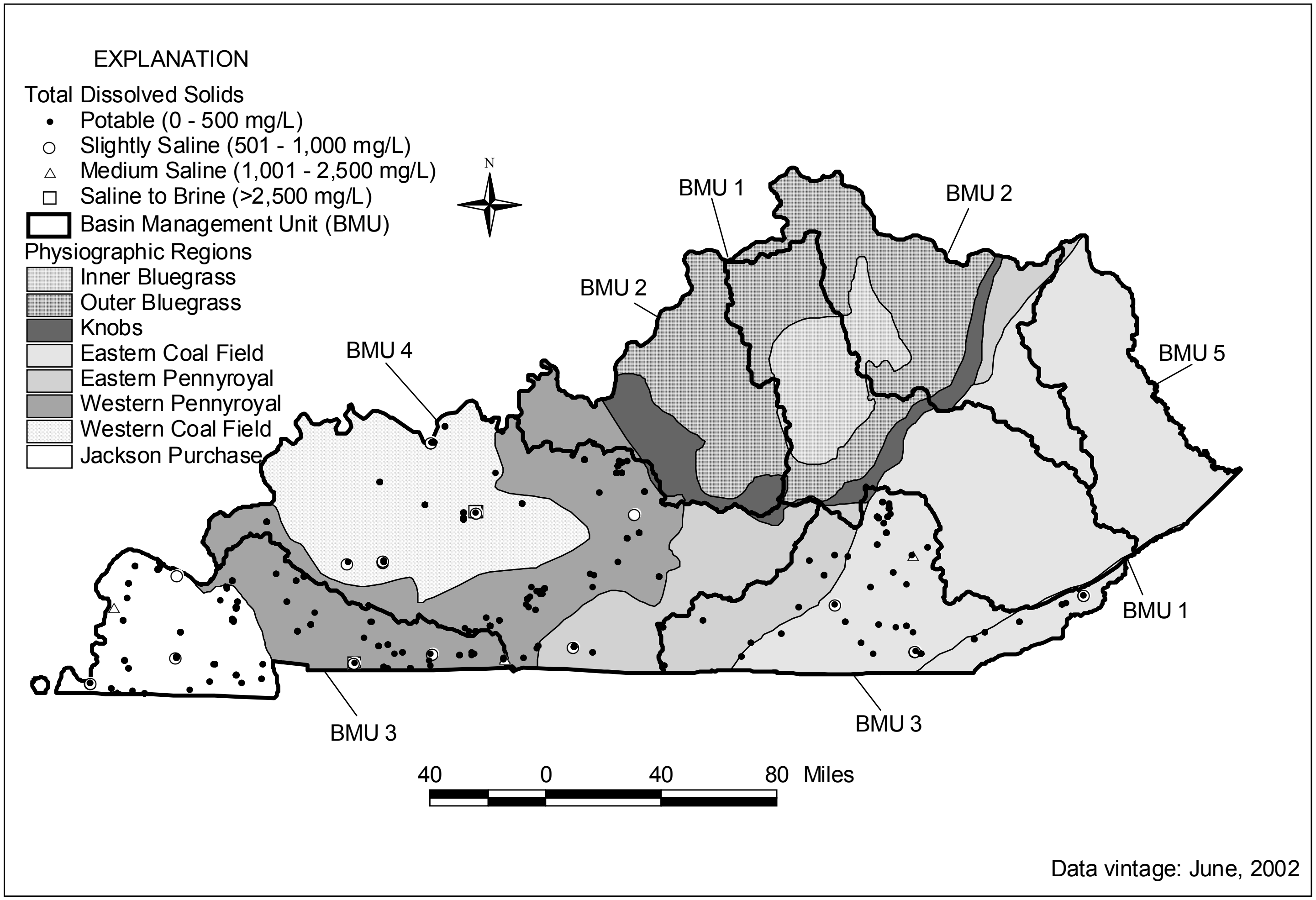


Figure 11. Sample sites and total dissolved solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

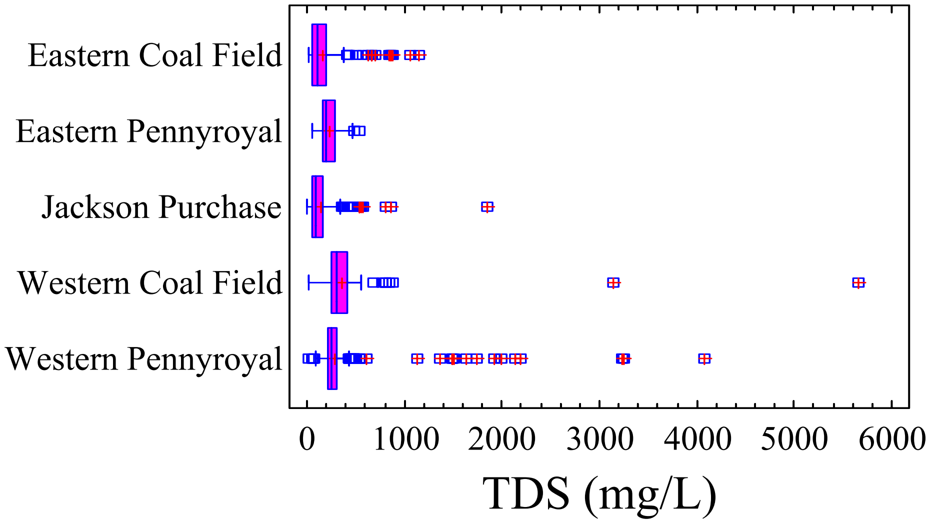


Figure 12. Summary plot for TDS measurements, grouped by physiographic region. SMCL = 500 mg/L.

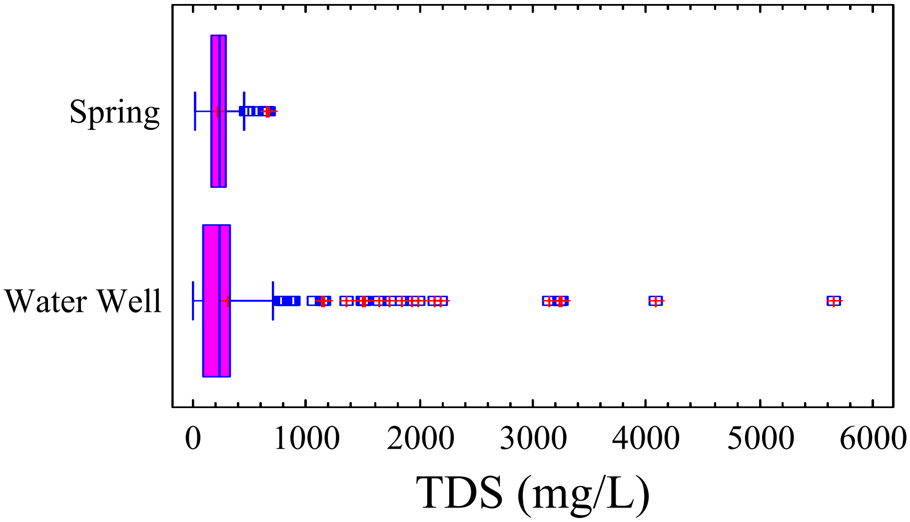


Figure 13. Summary of total dissolved solids values grouped by site type. SMCL = 500 mg/L.

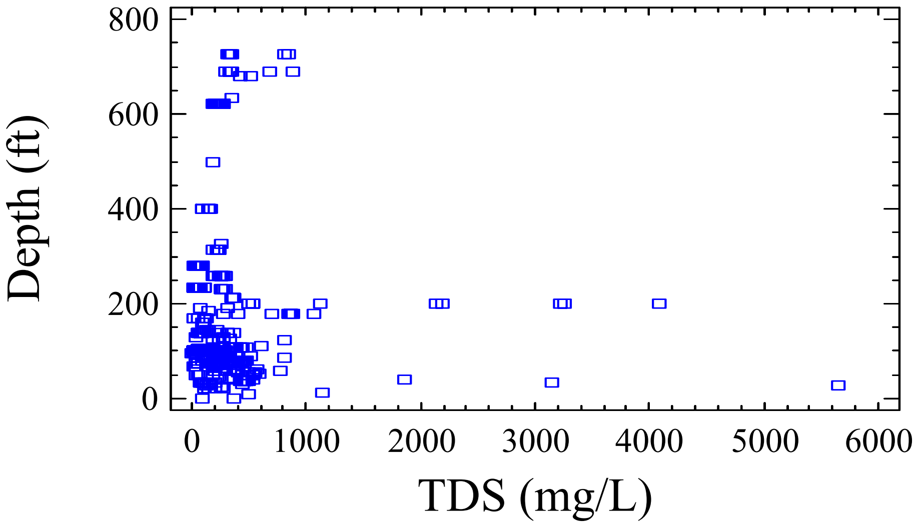


Figure 14. Plot of total dissolved solids values versus well depth. SMCL = 500 mg/L.

Summary: More than 95 percent of the reported TDS values in the project area are less than 500 mg/L. Values higher than 500 mg/L are found in the Eastern Coal Field, the Western Pennyroyal Region in the Lower Cumberland watershed, and the Western Coal Field in the Green River watershed. Some high-TDS values in the Eastern Coal Field may represent groundwater discharge from deep, regional flow systems (Wunsch, 1993). In the Western Coal Field and Western Pennyroyal Regions, high TDS values may be naturally occurring (Hopkins, 1966) or caused by brines from nearby oil and gas production wells.

Specific Electrical Conductance

Specific electrical conductance, also referred to as conductivity, is a measure of the ease with which water conducts an electrical current. It is an indirect measure of water quality and is proportional to total dissolved solids concentrations. 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, calcium and bicarbonate).

Conductance or conductivity is reported in micromhos per centimeter at a standard temperature, usually 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 11,291 conductance measurements from sites in BMU's 3 and 4. This extremely large number of measurements is the result of the extensive field sampling program associated with the NURE project (Smith, 2001). Values range from zero to 178,000 microsiemens per centimeter and sample depths range to 4,100 feet (Fig. 15). Samples from depths greater than 730 feet were collected and reported as part of a large USGS program that surveyed water quality in all accessible wells in the area. 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 DOW and identified as a water well was 730 feet. 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 feet from this summary. The resulting data set is summarized in Table 6. Maximum and minimum conductance values are similar in BMU's 3 and 4; however, the first quartile, median, and third quartile values of conductance are lower in BMU 3 than in BMU 4.

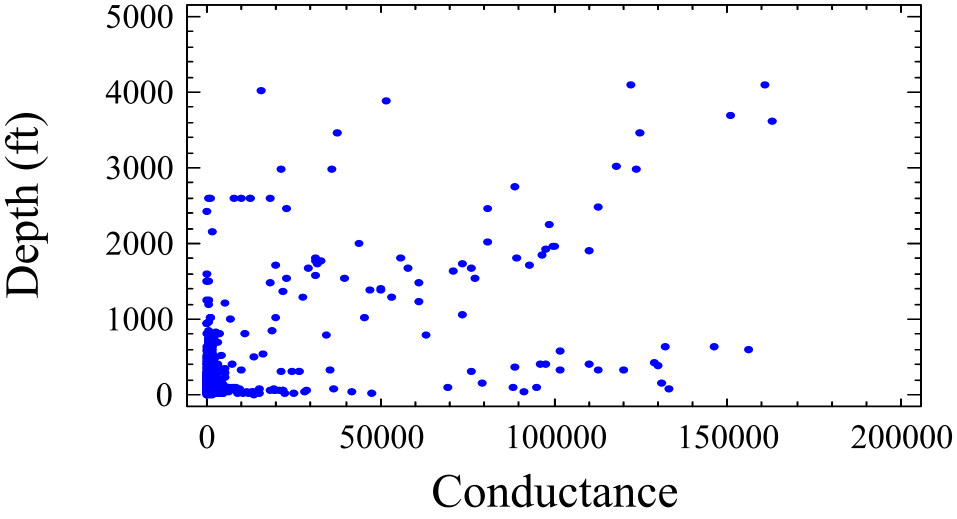


Figure 15. Plot of conductance (microsiemens/cm) versus depth.

Table 6. Summary of conductance measurements (microsiemens/cm).

	BMU 3	BMU 4
Number of measurements	5,100	6,015
Number of sites	3,296	4,166
Maximum	178,000	168,000
3rd quartile	410	670
Median	269	393
1st quartile	128	246
Minimum	3.4	2.5
Interquartile range	128 to 410	246 to 670

Cumulative data plots (Figs. 16 and 17) show that the distribution of conductance values is similar in BMU's 3 and 4. However, grouping the data by major river watershed (Fig. 18), mapping the values (Fig. 19), and grouping the data by physiographic region (Fig. 20) shows variations within each BMU. High conductance values occur throughout BMU 4, but are restricted to the eastern part of BMU 3. The high values in BMU 3 are almost entirely from sites in the Eastern Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland River watershed (Figs. 19 and 20). There are no values greater than 10,000 microsiemens per centimeter in the Lower Cumberland or Tennessee River watersheds of BMU 3, and very few in the Jackson Purchase area; however, values exceeding 10,000 microsiemens are common in the Upper Cumberland, Green, and Tradewater River Basins (Figs. 18 and 19).

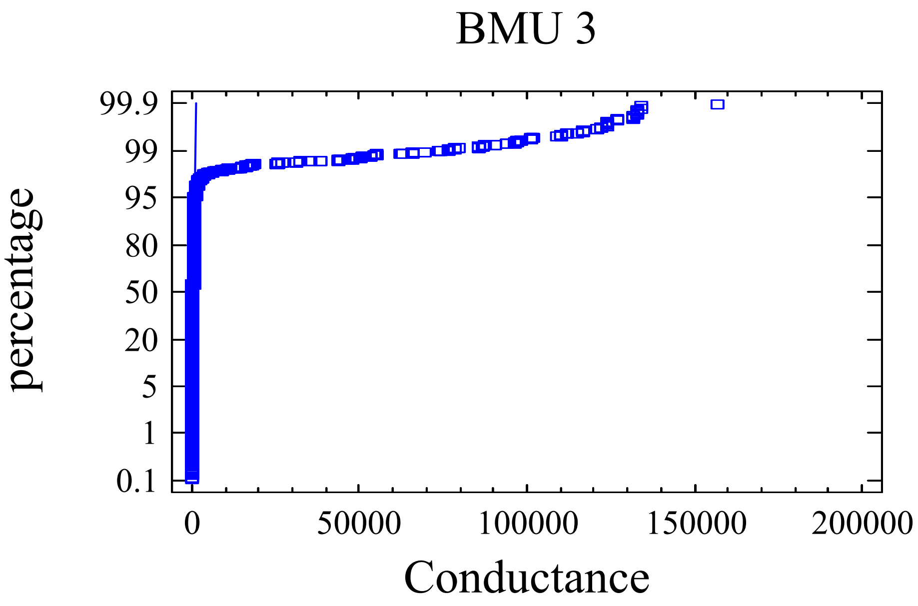


Figure 16. Cumulative plot of conductance (microsiemens/cm) for groundwater samples from basin management unit 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

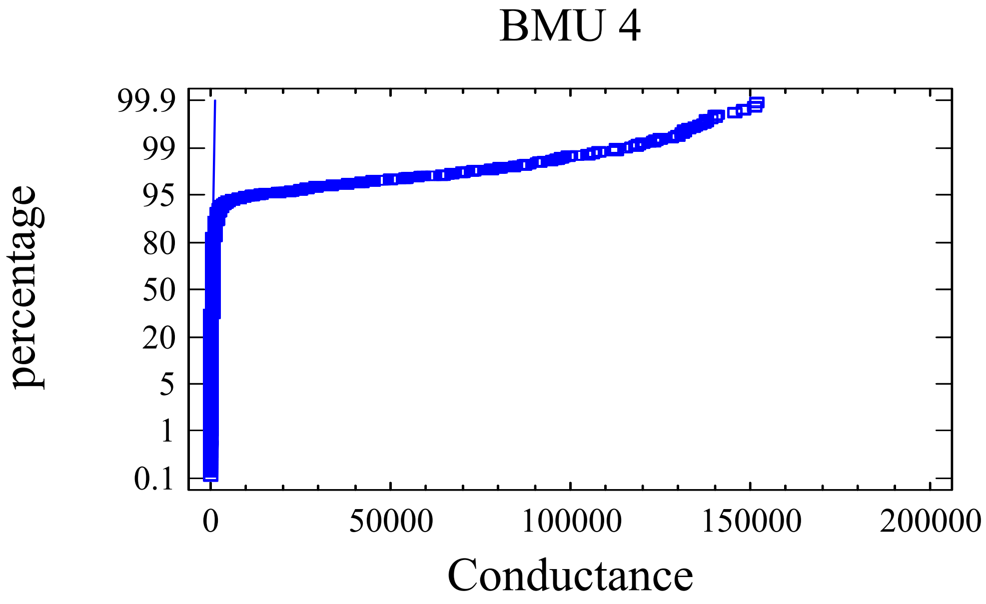


Figure 17. Cumulative plot of conductance (microsiemens/cm) for groundwater samples from basin management unit 4. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

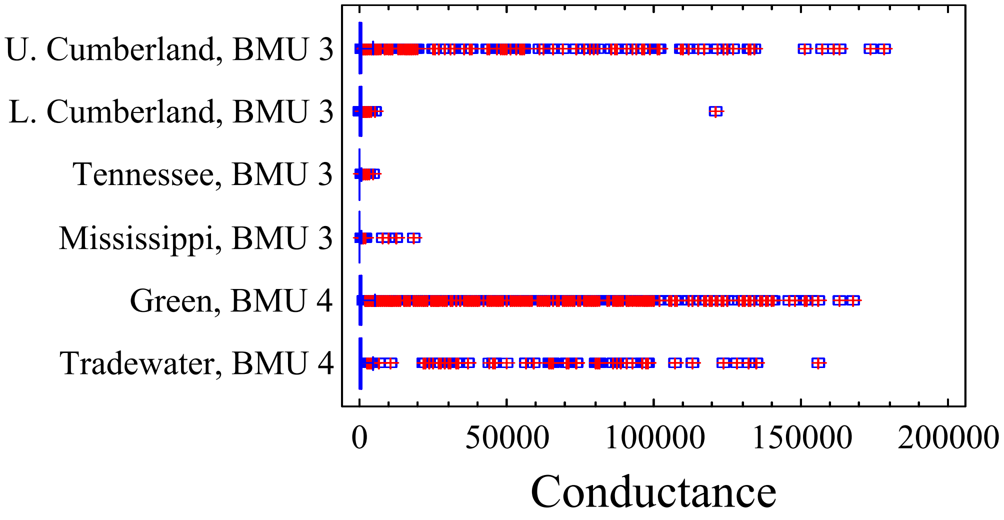
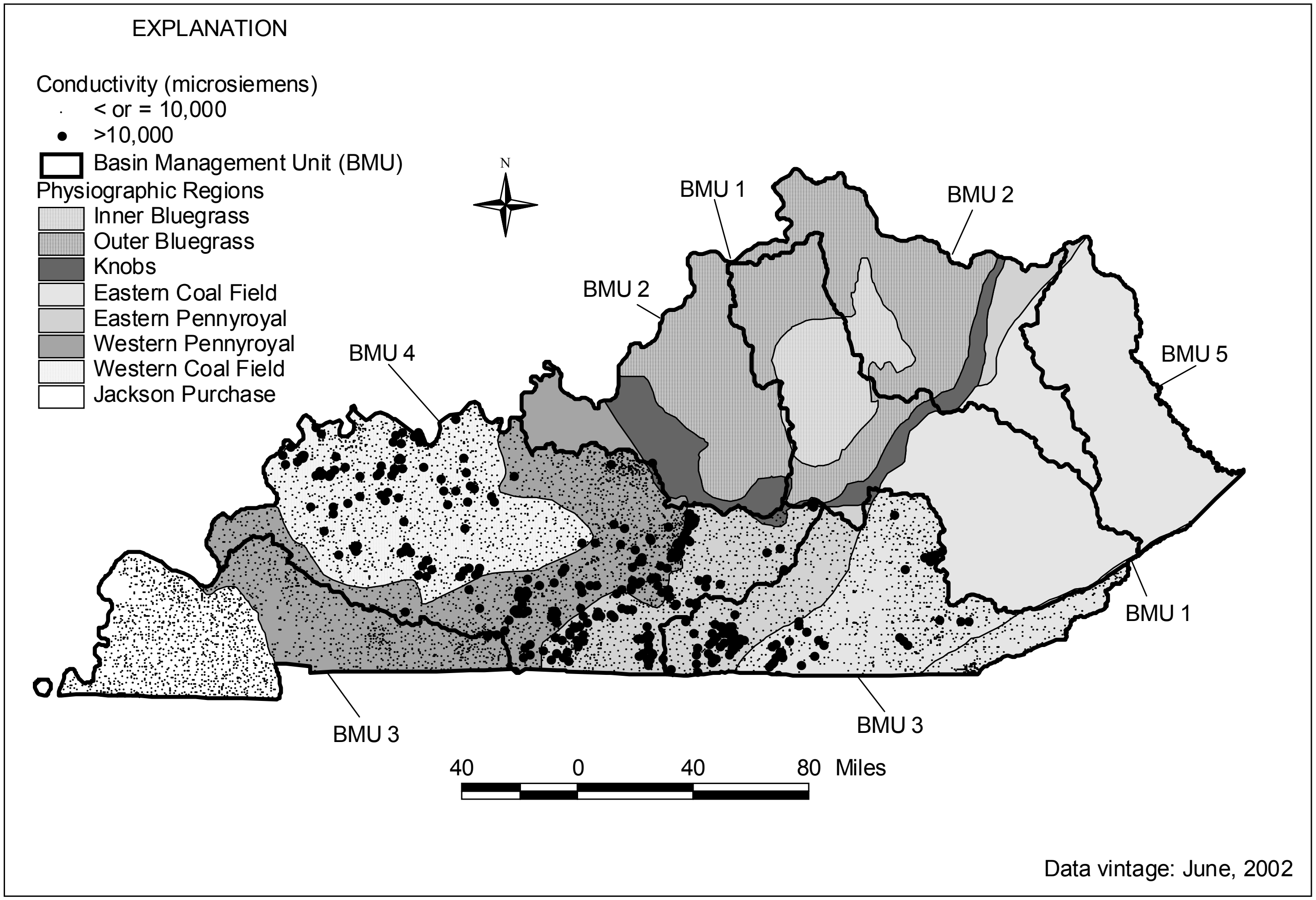


Figure 18. Summary of conductance data (microsiemens/cm) grouped by major river watershed.



Data vintage: June, 2002

Figure 19. Sample sites and conductance values.

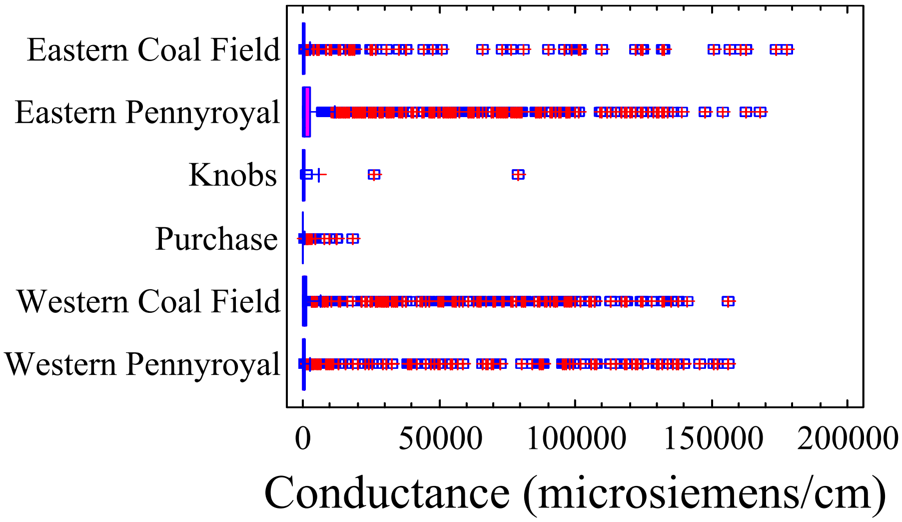


Figure 20. Summary of conductance measurements grouped by physiographic region.

A band of high-conductivity values along the boundary between the Eastern and Western Pennyroyal Regions (Fig. 19) generally follows the Dripping Springs Escarpment, as shown by Brown and Lambert (1963). This escarpment separates the topographically higher Mammoth Cave Plateau to the north and west from the lower plateau of the Pennyroyal Plain (terminology of Brown and Lambert, 1963). The escarpment also marks the boundary between Late Mississippian Chesterian series strata (alternating limestone, sandstone, and shale) beneath the Mammoth Cave Plateau and Late Mississippian Osagean, Meramecian, and lower Chesterian strata (relatively pure limestone) beneath the Pennyroyal Plain. The escarpment may focus the discharge of groundwater from deeper flow systems along the boundary between the Eastern and Western Pennyroyal. Mississippian limestones in this region all contain abundant pyrite (Brown and Lambert, 1963). Discharge of sulfate-rich, brackish to moderately saline groundwater from beneath the Western Coal Field or the Mammoth Cave Plateau is a probable cause of the observed conductivity values along the Eastern Pennyroyal–Western Pennyroyal boundary.

The highest conductance values are found in groundwater from wells rather than springs (Fig. 21). No relation between conductance values and well depth was observed.

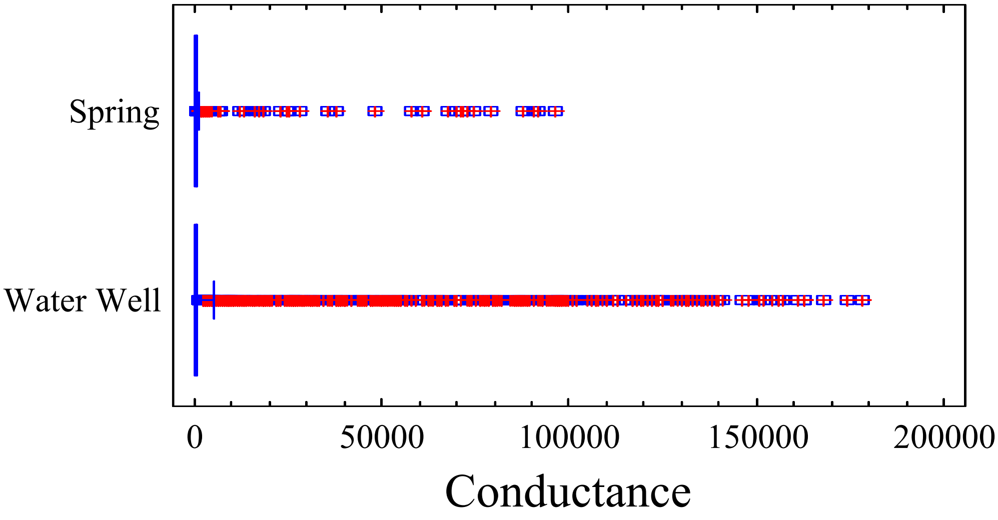


Figure 21. Summary of conductance measurements (microsiemens/cm) grouped by site type.

Summary: Conductance values as high as 178,000 microsiemens/cm have been reported in water wells in the project area. Some of these reports are for wells deeper than 730 feet, which may be exploration wells or oil and gas wells that are improperly identified as water wells. Only approximately half the reported conductance values also have well depths. Therefore, it is possible that some of the high conductance values reported for water wells were actually measured in deeper wells that are not used for domestic or municipal water supplies. Nevertheless, there are many high conductance values in samples from depths less than 730 ft.

The depth range of wells is approximately the same throughout the project area. However, many sites in the Upper Cumberland, Green, and Tradewater River Basins produce water that exceeds 10,000 microsiemens/cm, whereas no sites in the Tennessee River Basin or the Jackson Purchase exceeded 10,000 microsiemens/cm, and only one site in the Lower Cumberland River Basin exceeded 10,000 microsiemens/cm. The existing data therefore suggest that NPS contamination, possibly from improperly constructed or abandoned oil and gas wells, has affected groundwater in this area.

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:

$$\text{Hardness (mg/L calcium carbonate equivalent)} = 2.5\ \text{Ca (mg/L)} + 4.1\ \text{Mg (mg/L)} \qquad (1)$$

A frequently used classification of hardness in water supplies is shown in Table 7 (U.S. Geological Survey Web site, water.usgs.owq/explanation.html).

Table 7. Hardness classification of water supplies.

Hardness Category	**Concentration (mg/L)**
Soft	0 to 17
Slightly hard	18 to 60
Moderately hard	61 to 120
Hard	121 to 180
Very hard	more than 180

Calcium and magnesium concentrations from the data repository were combined according to equation (1) to produce a total of 1,769 groundwater hardness values at 591 sites in BMU 3 and 12,560 values at 895 sites in 4 (Table 8). Very hard water is the predominant type in each BMU. Soft to moderately hard water is more common in BMU 3 than in BMU 4; very hard water is more common in BMU 4 than in BMU 3 (Table 8).

Table 8. Summary of hardness measurements (mg/L).

	BMU 3	**BMU 4**
Number of values	1,769	2,560
Number of sites	591	895
% soft	12.0	3.9
% slightly hard	20.1	6.7
% moderately hard	11.3	8.2
% hard	12.5	11.5
% very hard	44.0	69.7

Cumulative data plots (Figs. 22 and 23) are generally similar for BMU’s 3 and 4.

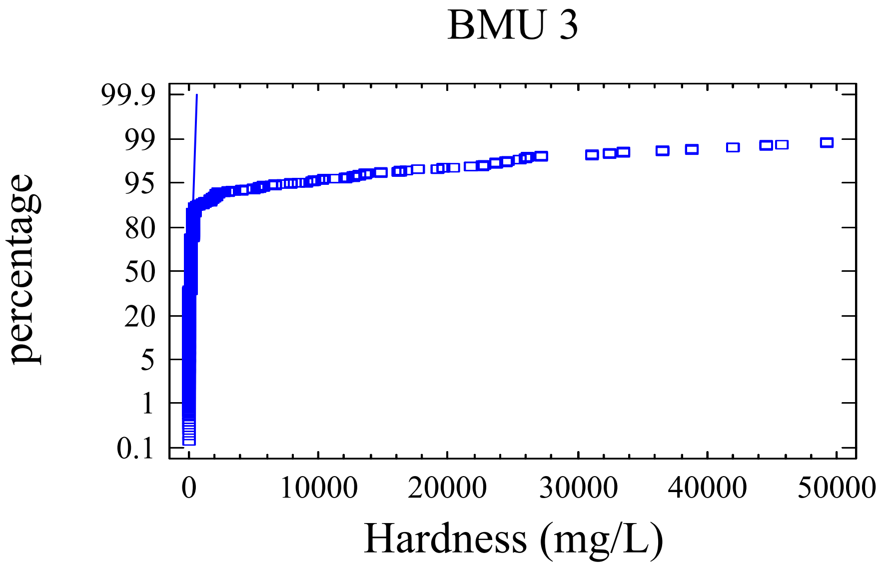


Figure 22. Cumulative plot of hardness values in BMU 3. Values greater than 50,000 mg/L have been omitted to better show the majority of the data.

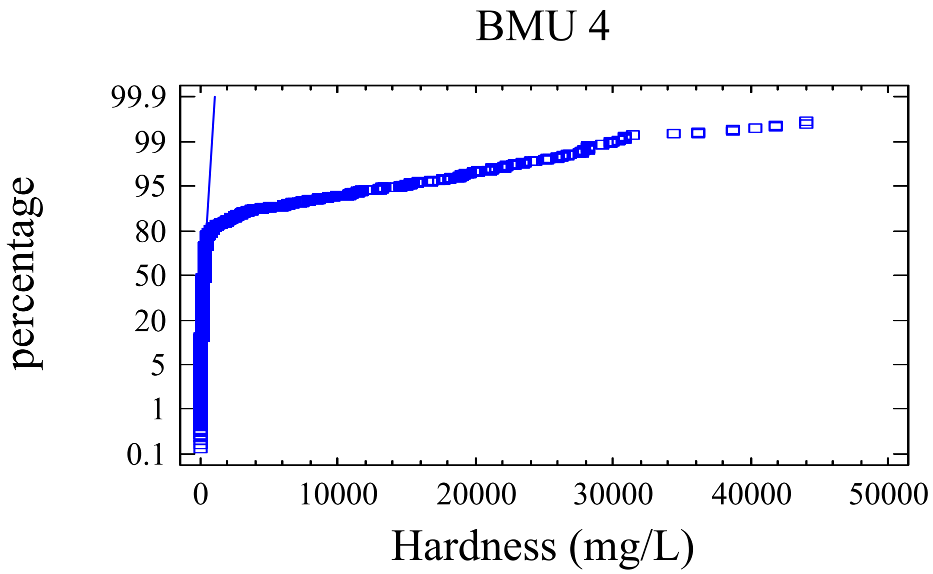


Figure 23. Cumulative plot of hardness values in BMU 4. Values greater than 50,000 mg/L have been omitted to better show the majority of the data.

Figure 24 shows that sites in the western part of BMU 3 (Lower Cumberland, Tennessee, and Mississippi River watersheds) are generally low, whereas sites in the eastern part of BMU 3 (Upper Cumberland River watershed), and throughout BMU 4 (Green and Tradewater River watersheds) reach very high hardness levels.

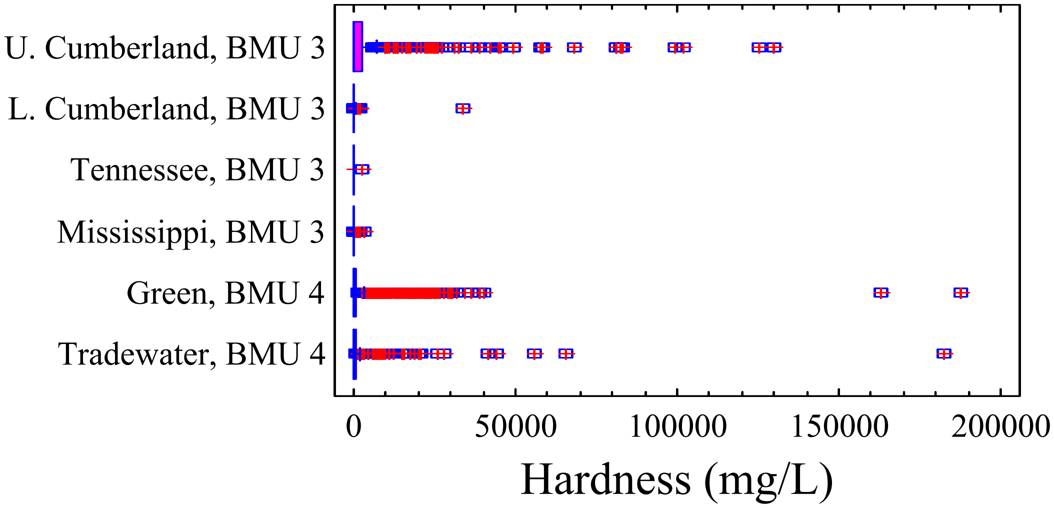


Figure 24. Summary of hardness values grouped by major river watershed.

A map (Fig. 25) and a summary of data grouped by physiographic region (Fig. 26) show that soft water (low hardness values) is most common in the Jackson Purchase Region.

The highest hardness values are found in groundwater from water wells rather than from springs (Fig. 27). No trend of hardness with water well depth was observed. Very high hardness values (> 50,000 mg/L as $CaCO_3$) occur mainly in the Upper Cumberland, Green, and Tradewater watersheds. These high values may be affected by deep, saline water in the Eastern Coal Field (Upper Cumberland River watershed) and brines from oil and gas production in the Western Coal Field and Pennyroyal Regions (Green and Tradewater watersheds).

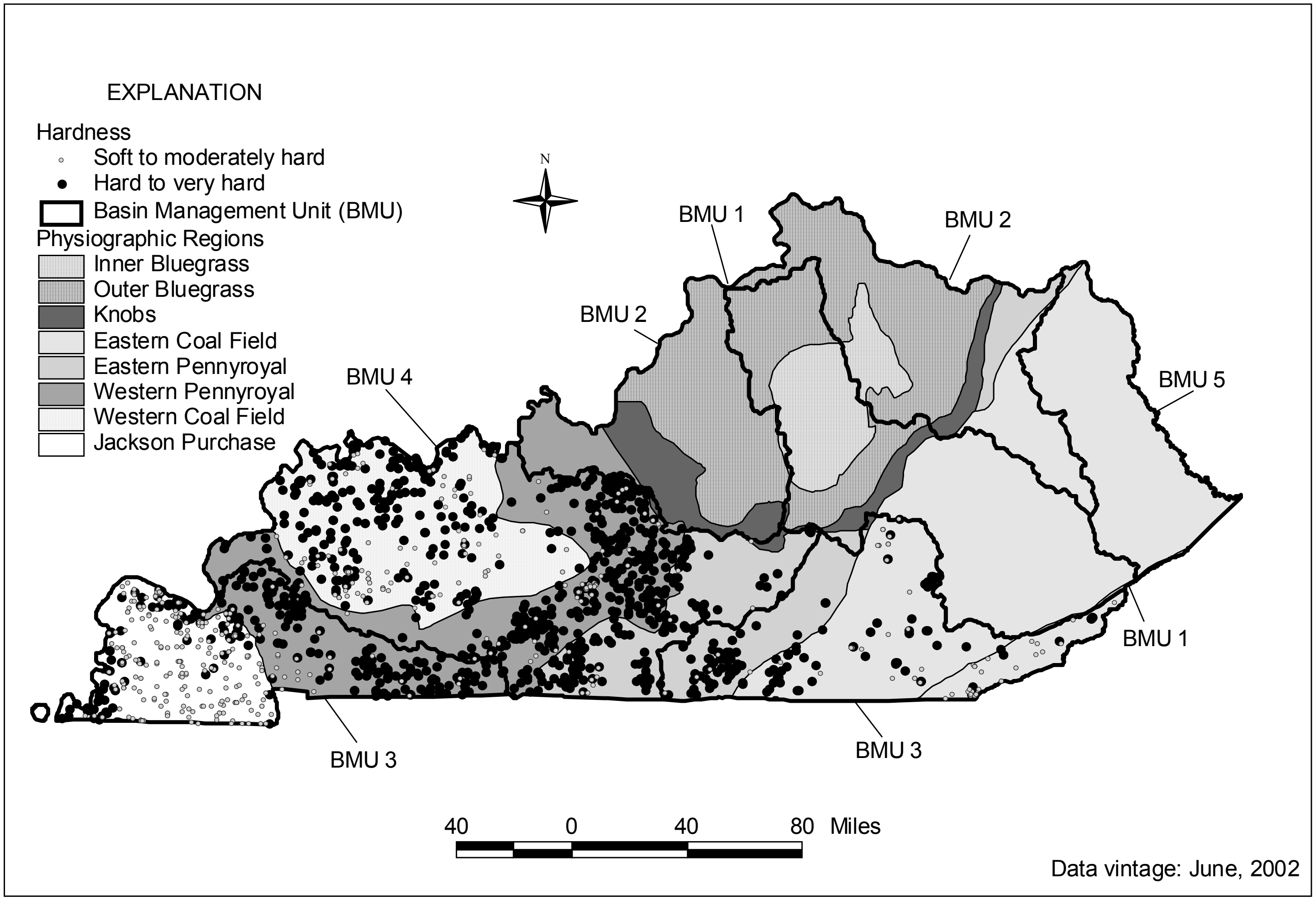


Figure 25. Sample sites and hardness values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

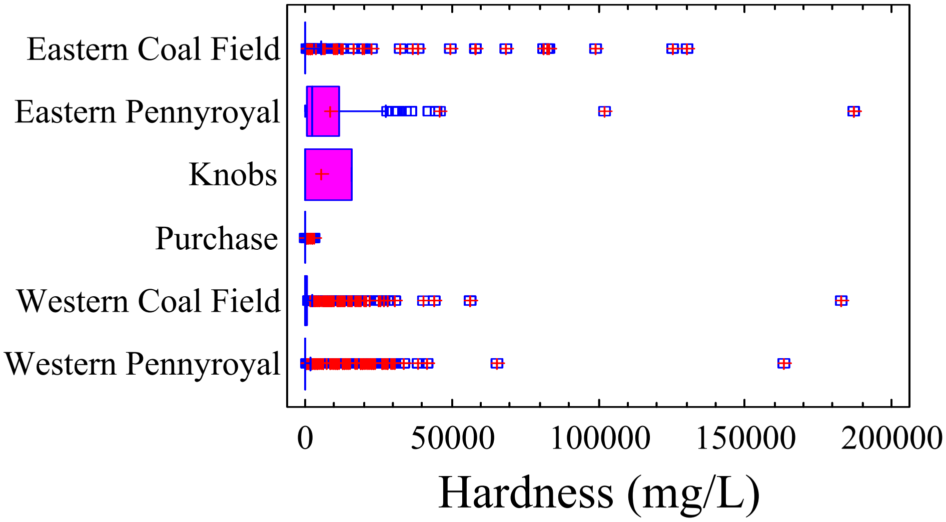


Figure 26. Summary plot of hardness values for groundwater grouped by physiographic region.

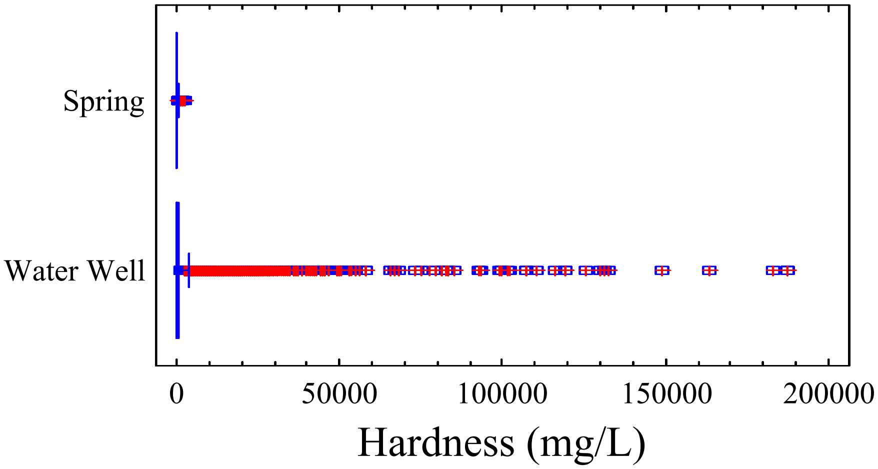


Figure 27. Summary of hardness values grouped by site type.

Summary: Hard to very hard groundwater is predominant throughout the project area, with the exception of wells in the sandy, poorly consolidated Jackson Purchase Region. In both the coal fields and the Pennyroyal carbonate terrain, dissolved calcium and magnesium supplied by calcite and dolomite result in 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 Coal Field and Pennyroyal Regions, indicating high calcium and magnesium concentrations, may be the result of water-well contamination from deeper, saline fluids.

Total Suspended Solids

Suspended particulate material is reported as total suspended solids (TSS). Total suspended solids concentrations are typically higher in groundwater samples from karst springs where turbulent water flow can transport fine material such as clays and particulate organic material, from uncased wells that have been vigorously stirred during purging prior to sample collection, or from wells that intercept a fracture or karst conduit. 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. However, some metals and pesticides are preferentially sorbed onto or included in the matrix of suspended material, so water high in total suspended solids may also contain important 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 TSS levels be less than 35 mg/L.

In BMU's 3 and 4 there are 576 and 741 measurements of total suspended solids, respectively. The values range from 0 to 1,354 mg/L (Table 9). Despite the high maximum values in each BMU, the median and interquartile range of TSS values is very low for both BMU 3 and BMU 4. Eighty percent of the total suspended solids measurements are less than 10 mg/L, and 90 percent of the measurements are less than 20 mg/L.

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

	BMU 3	**BMU 4**
Number of values	576	741
Number of sites	101	80
Maximum	442	1,354
3rd quartile	4	9
Median	3	3
1st quartile	3	3
Minimum	0	0
Interquartile range	3 to 4	3 to 9

Cumulative data plots (Figs. 28 and 29) show the prevalence of low TSS values in both BMU's 3 and 4. The plots also show that high TSS values are more common in BMU 4.

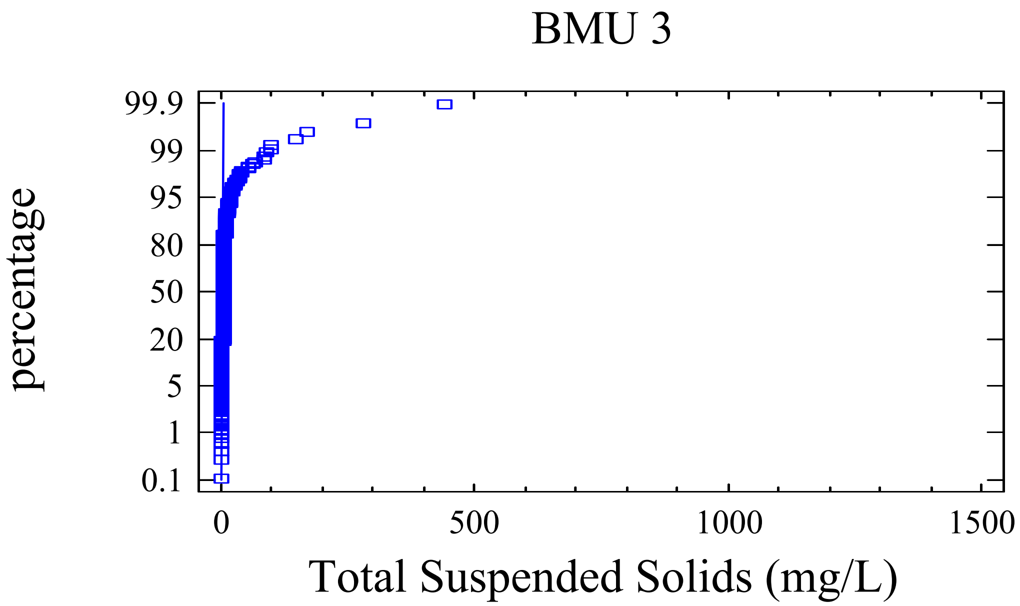


Figure 28. Cumulative plot of total suspended solids values from BMU 3.

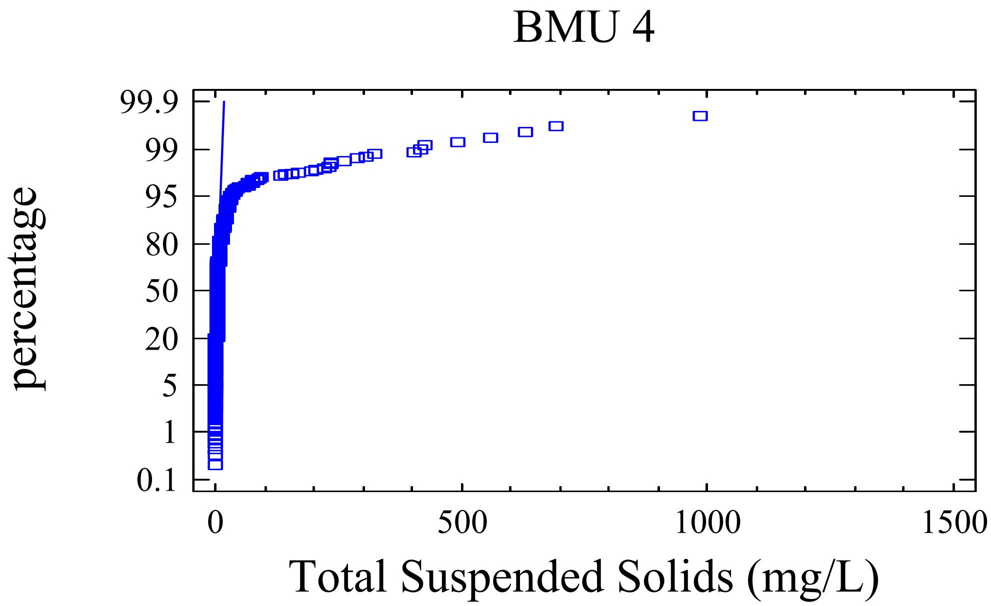


Figure 29. Cumulative plot of total suspended solids values from BMU 4.

Grouping the results by major watershed (Fig. 30) shows that the lowest values are from sites in watersheds of tributaries to the Mississippi River in BMU 3, whereas the highest values are from sites in the Green and Tradewater River Basins of BMU 4.

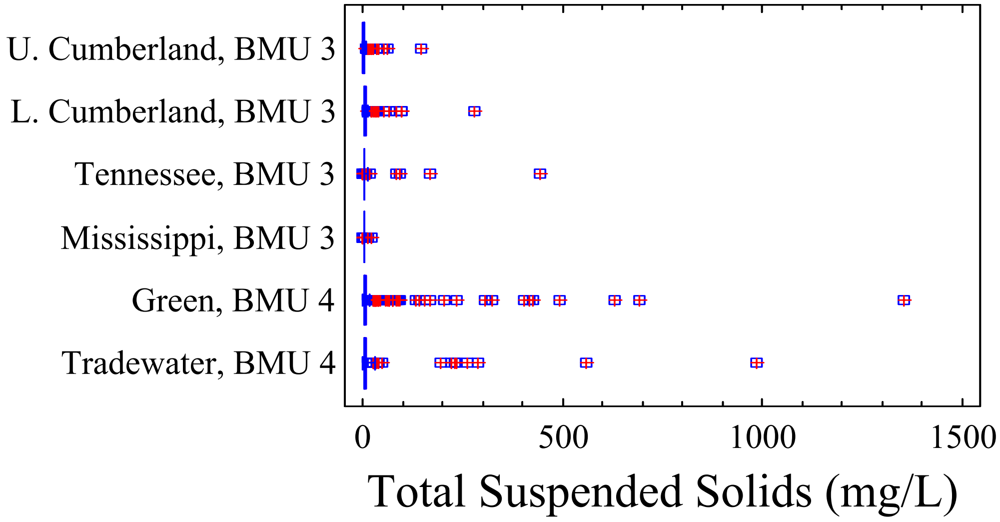


Figure 30. Summary of total suspended solids data grouped by major river watershed.

A map (Fig. 31) shows a band of high total suspended solids values in the Western Pennyroyal Region in watersheds of the Lower Cumberland and Green Rivers. Although there are many high values reported from the Jackson Purchase (Fig. 32), the map shows that these values are from only two sites.

Both wells and springs produce groundwater with high total suspended solids (Fig. 33). Total suspended solids values are generally higher in water from shallow wells (less than 200 feet) than from deeper wells (Fig. 34). These observations, together with the mapped distribution of sites having high TSS values, suggest that springs and shallow wells in the Western Pennyroyal Region are likely to produce turbid water (as previously reported by Brown and Lambert, 1963), as are poorly cased wells in the Eastern Coal Field and the Jackson Purchase Region.

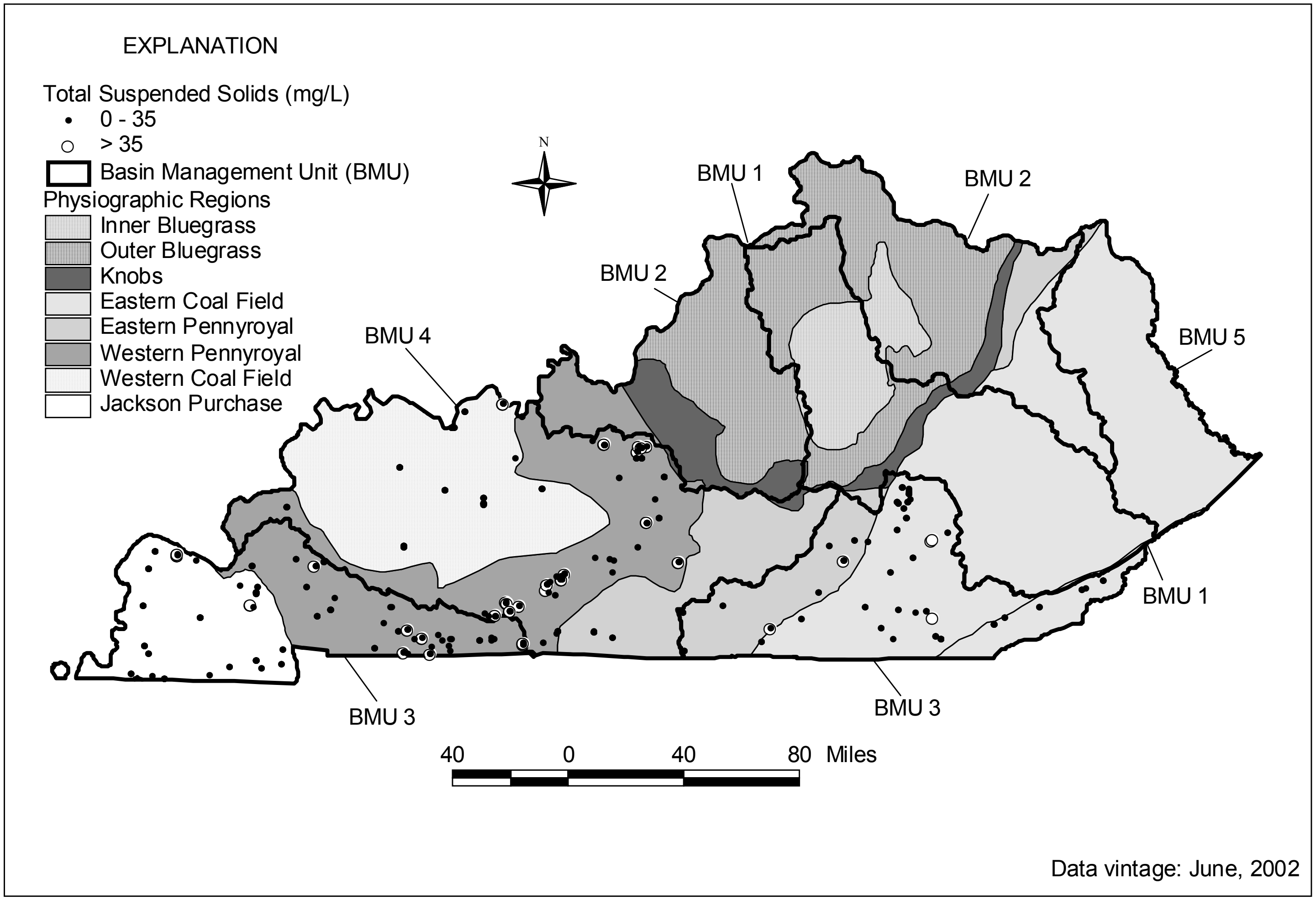


Figure 31. Sample sites and total suspended solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

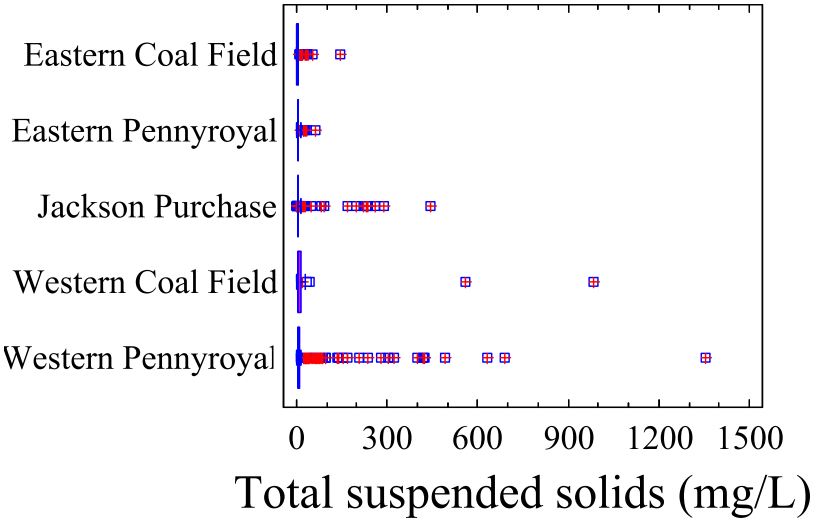


Figure 32. Summary plot of total suspended solids values grouped by physiographic region.

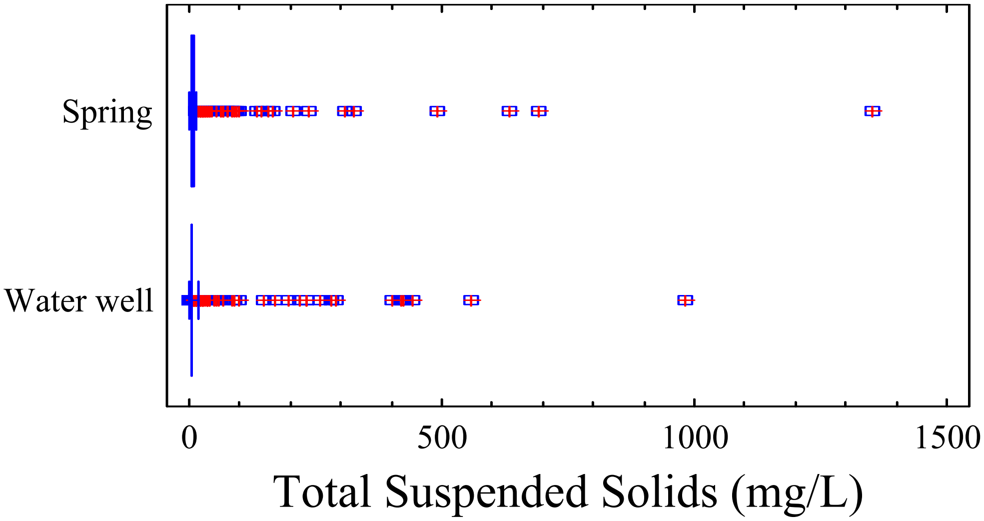


Figure 33. Summary plot of total suspended solids values grouped by site type.

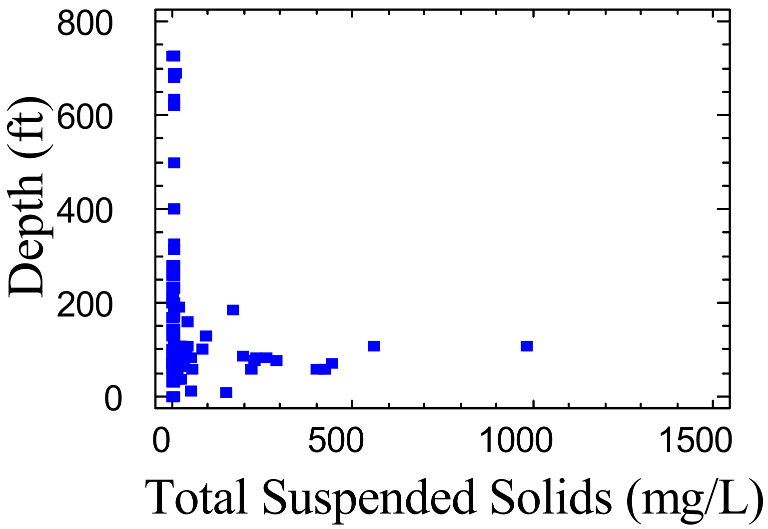


Figure 34. Plot of total suspended solids values versus well depth.

Summary: Total 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 some potentially toxic metals and synthetic organic chemicals are preferentially carried by suspended clays and organic material. The distribution of the highest TSS 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 and the lithologically heterogeneous Eastern Coal Field.

Inorganic Anions

Chloride

Chloride (Cl) is present in most natural groundwater at low to moderate amounts. It is a highly conservative anion; once in solution it is generally 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 deep, brackish groundwater that is commonly encountered at depth in the coal fields and the Pennyroyal Region (Hopkins, 1966; Wunsch, 1993). NPS 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 (SMCL) of 250 mg/L for chloride because water containing more than this amount has an unpleasant taste that makes it unsuitable for domestic use.

The data repository contained 15,492 chloride measurements from sites in BMU's 3 and 4. Values as high as 141,000 mg/L and sample depths as great as 4,200 feet have been reported. High chloride concentrations are present in both shallow and deep wells (Fig. 35). As with the conductance data discussed previously, chloride results from wells deeper than 730 feet 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 141,000 mg/L exist in the project area, more than 96 percent of the samples in BMU 3 and more than 90 percent of the samples in BMU 4 contain less than 250 mg/L chloride. The median value is slightly lower in BMU 3 than in BMU 4, and the interquartile range is smaller in BMU 3 than in BMU 4 (Table 10).

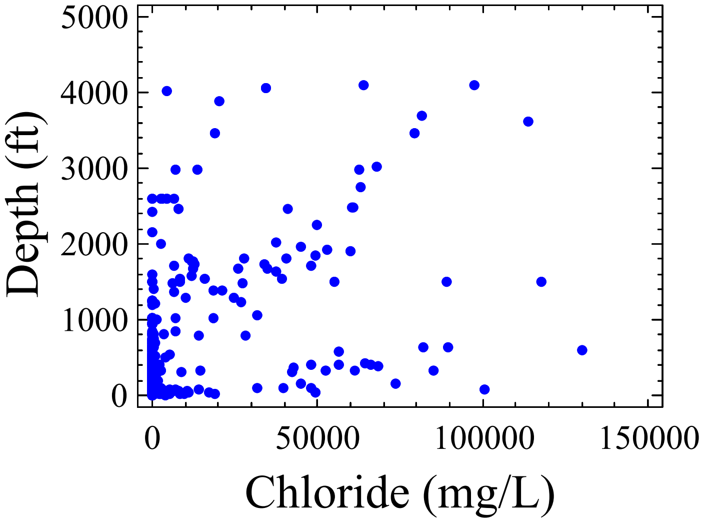


Figure 35. Plot of chloride measurements versus depth (feet). SMCL = 250 mg/L.

Table 10. Summary of chloride measurements (mg/L).

Parameter	**BMU 3**	**BMU 4**
Measurements	6,762	8,472
Sites	2,270	2,178
Maximum	130,000	141,000
3rd quartile	11.6	30.0
Median	5.8	9.2
1st quartile	3.0	4.0
Minimum	0.0	0.0
% values < 250	96.2	90.0
Interquartile range	3.0 to 11.6	4.0 to 30.0

SMCL = 250 mg/L

Cumulative data plots (Figs. 36 and 37) show fewer high values in BMU 3 than in BMU 4. As was the case for conductance and hardness, the similarity in chloride values between the large basin management units masks the differences within the basin management units.

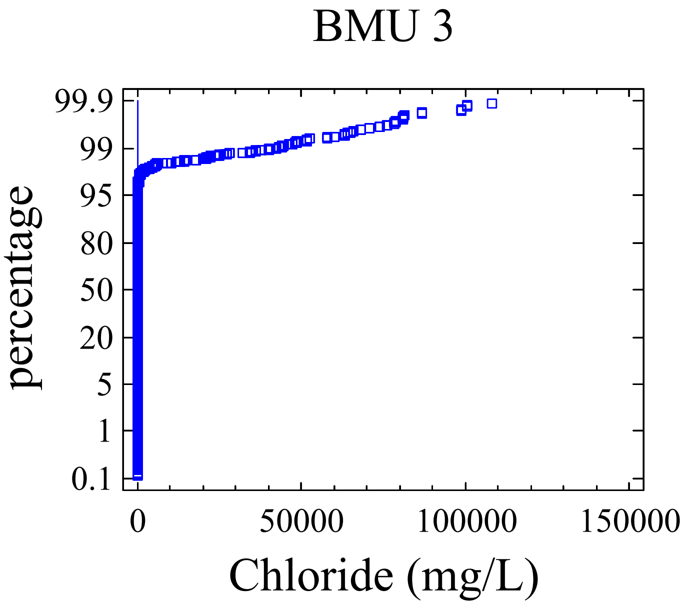


Figure 36. Cumulative plot of chloride values in BMU 3. SMCL = 250 mg/L. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

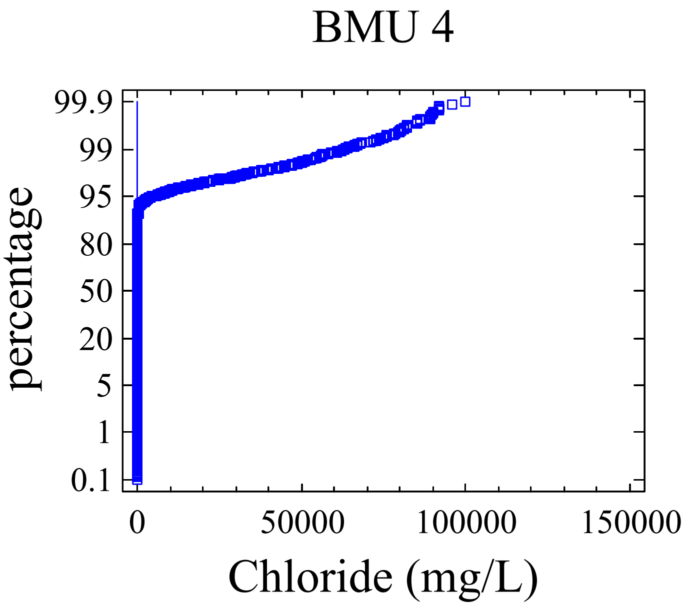


Figure 37. Cumulative plot of chloride values in BMU 4. SMCL = 250 mg/L. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Grouping the results by major watershed (Fig. 38) shows that only the Upper Cumberland watershed in BMU 3 contains sites where high chloride concentrations were commonly reported, whereas both the Green and Tradewater watersheds in BMU 4 contain wells and springs with high chlorinity.

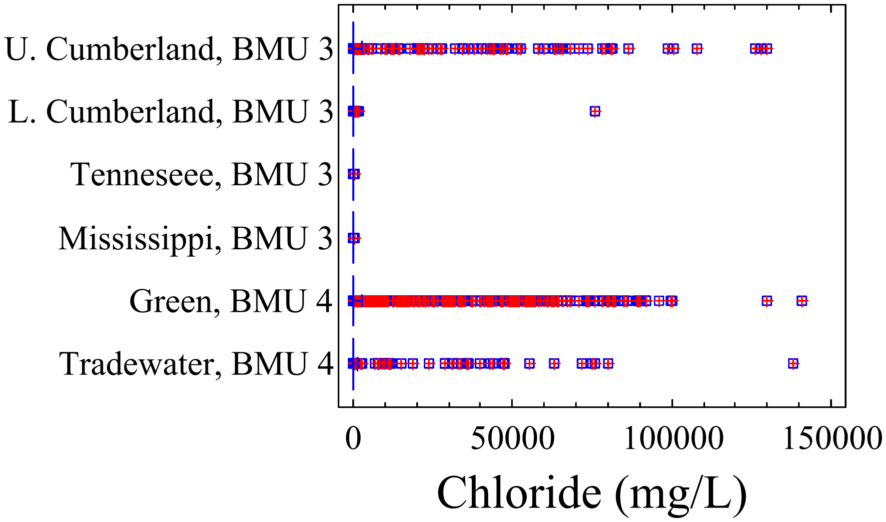


Figure 38. Summary of chloride values grouped by major watersheds. SMCL = 250 mg/L.

Figure 39 shows that chloride concentrations greater than 250 mg/L have the same distribution as did high conductance values (Fig. 19). Sites having chloride concentrations greater than 250 mg/L are common in the Eastern Pennyroyal Region of the Upper Cumberland watershed in BMU 3 and the Western Pennyroyal and Western Coal Field Regions of the Green River watershed in BMU 4 (Figs. 39 and 40). Only sites in the Knobs and Jackson Purchase Regions lack very high chloride concentrations in groundwater samples. Groundwater from wells is more likely to have very high chloride concentrations than groundwater from springs. (Fig. 41).

As with conductivity measurements (Fig. 19), a band of high-chloride values occurs along the boundary between the Eastern and Western Pennyroyal Regions, generally following the Dripping Springs Escarpment (Brown and Lambert, 1963). This escarpment separates the topographically higher Late Mississippian Chesterian series strata (alternating limestone, sandstone, and shale) from the Late Mississippian Osagean, Meramecian, and lower Chesterian strata (relatively pure limestone). The escarpment could focus the discharge of groundwater from deeper flow systems along the boundary between the Eastern and Western Pennyroyal. Discharge of brackish to moderately saline groundwater from beneath the Western Coal Field or the Mammoth Cave Plateau is a probable cause of the observed chloride values along the Eastern Pennyroyal–Western Pennyroyal boundary.

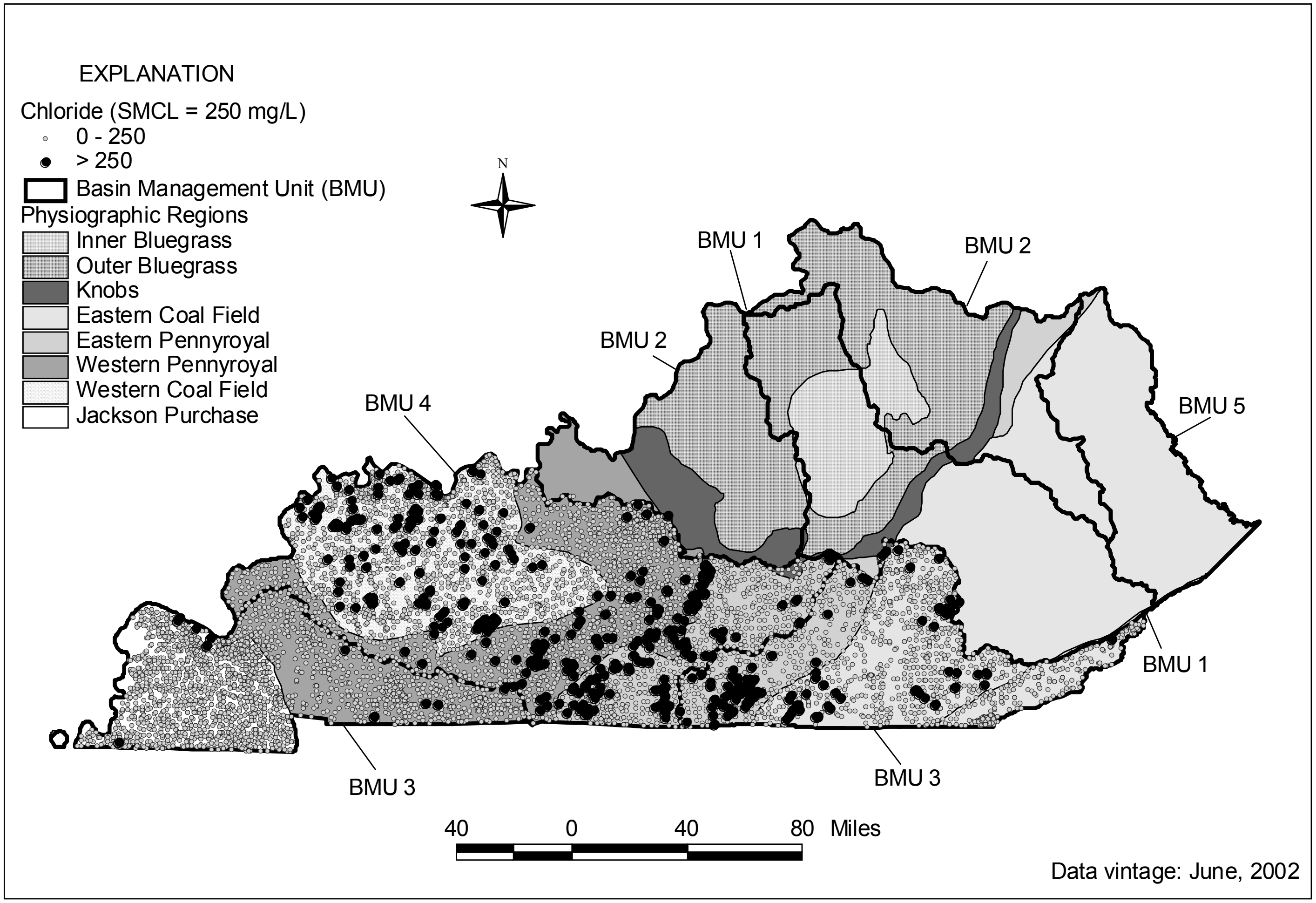


Figure 39. Sample sites and chloride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

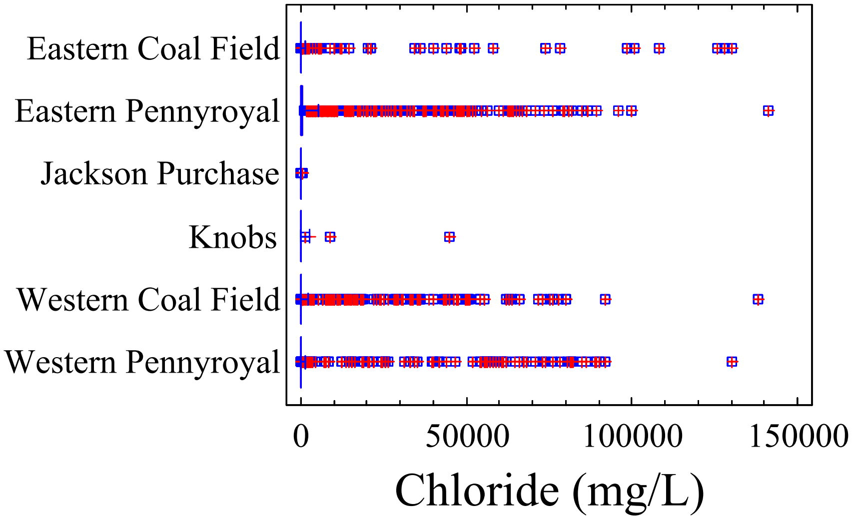


Figure 40. Summary of chloride concentrations grouped by physiographic region. SMCL = 250 mg/L.

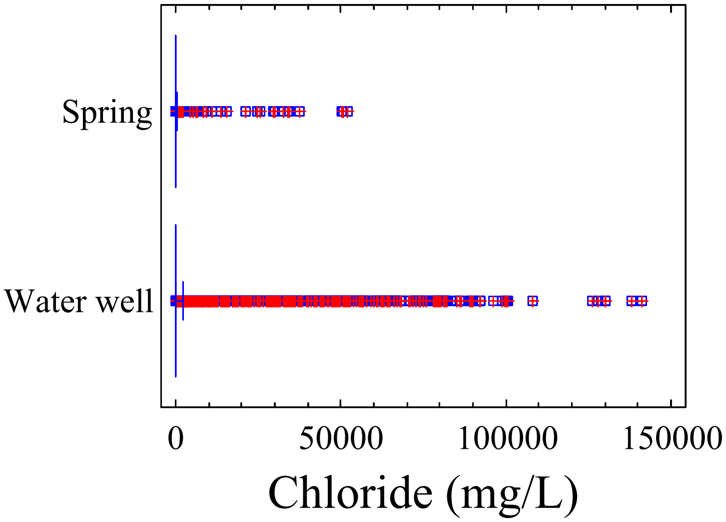


Figure 41. Summary of chloride concentrations grouped by site type. SMCL = 250 mg/L.

Summary: More than 90 percent of the reported chloride concentrations are less than 250 mg/L throughout the project area. However, a large number of sites produce groundwater that exceeds this level, particularly in the Eastern Pennyroyal Region of BMU 3 and the Western Pennyroyal and Western Coal Field of BMU 4. High-chlorinity groundwaters are more common from wells than from springs. Chloride values exceeding 100,000 mg/L have been reported from “water wells” at depths that are either less than 730 feet or were unreported. These samples may be from sites that are contaminated from leaking oil or gas wells or by other NPS sources; further investigations are needed to determine the source of the chlorinity at each site.

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 (SMCL) 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 reports is similar to that for conductance and chloride: many sites that are identified as water wells also have reported depths as great as 4,096 feet, and many sites do not have a well depth recorded. As in the cases of conductance and chloride, high sulfate concentrations were reported in samples from 730-foot depths and shallower. In this data summary we excluded any reports from depths greater than 730 feet because the deepest groundwater sample reported by the NREPC was 730 feet. Deeper wells are not likely to be used as groundwater supplies.

Table 11 summarizes sulfate data from groundwaters in basin management units 3 and 4. The highest value of 42,500 mg/L sulfate was reported from a spring in the Green River Basin. With the exception of this one value, all other sulfate concentrations in the data set are less than 10,000 mg/L. There are a large number of sites and measurements in both BMU's 3 and 4. BMU 4 concentrations exceed those from BMU 3 in all statistical measures except the minimum value, which is zero in both regions. BMU 4 has a larger interquartile range and a smaller percentage of values that are less than 500 mg/L and less than 250 mg/L than does BMU 3 (Table 11).

Cumulative data plots (Figs. 42 and 43) show there are many more high sulfate values (greater than 500 mg/L) in BMU 4 than in BMU 3.

Table 11. Summary of sulfate measurements (mg/L).

Parameter	**BMU 3**	**BMU 4**
Measurements	8,200	7,658
Sites	1,935	1,921
Maximum	3,840	42,500
3rd quartile	40	144
Median	11	22
1st quartile	5	8.4
Minimum	0	0
% values < 500	97.9	86.2
% values < 250	95.8	80.5
Interquartile range	5 to 40	8.4 to 144

SMCL = 250 mg/L

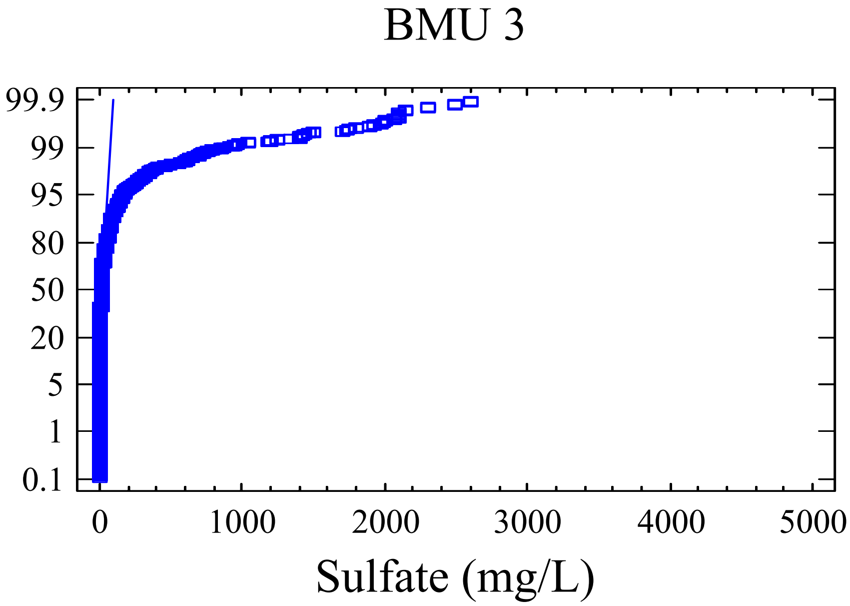


Figure 42. Cumulative plot of sulfate concentrations in BMU 3. SMCL = 250 mg/L. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

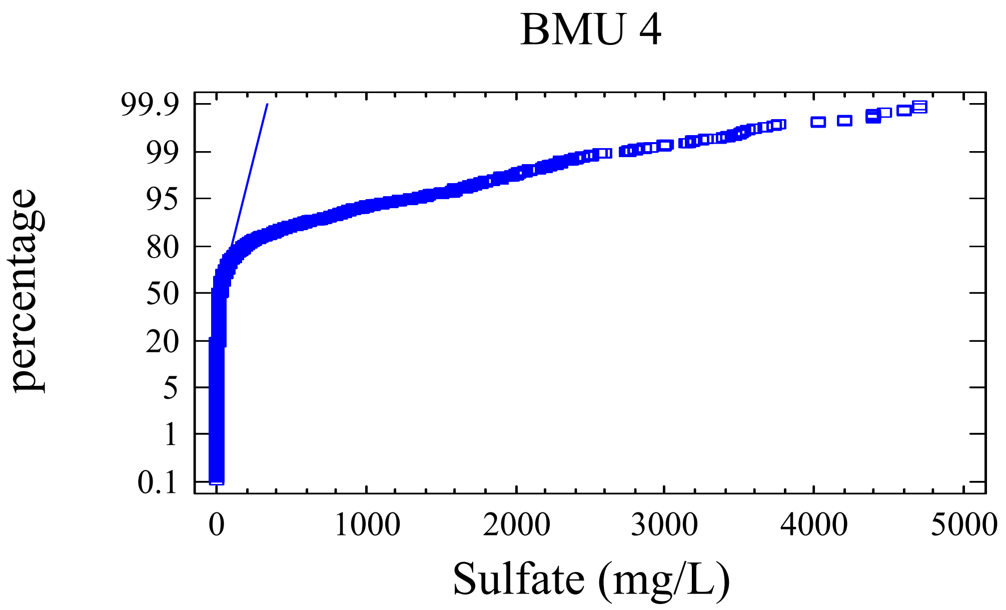


Figure 43. Cumulative plot of sulfate concentrations in BMU 4. SMCL = 250 mg/L. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Grouping the measurements by major watershed (Fig. 44) shows high sulfate concentrations in groundwater samples from all but the Mississippi River Basin in the western Jackson Purchase (Fig. 44).

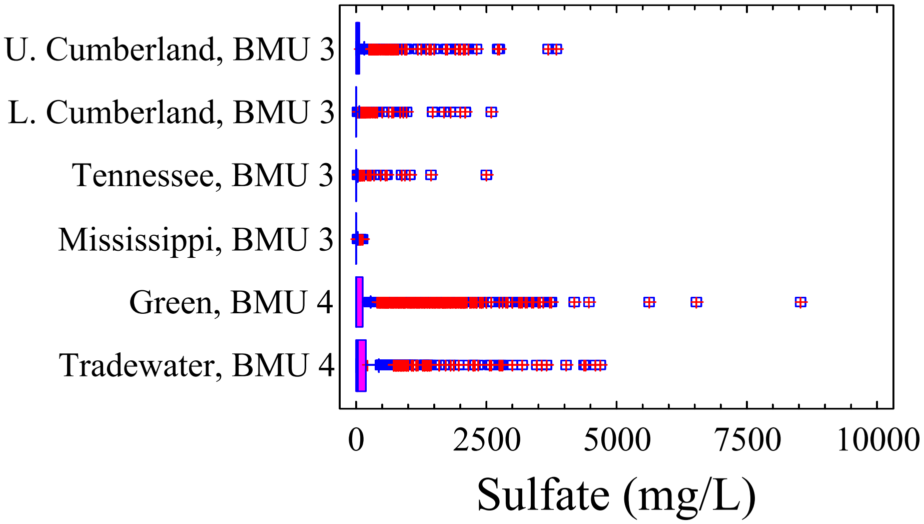


Figure 44. Summary of sulfate concentrations grouped by major watershed. SMCL = 250 mg/L.

A map (Fig. 45) and grouping measurements by physiographic region (Fig. 46) show that sites having sulfate values greater than 250 mg/L are relatively rare in the Lower Cumberland, Tennessee, and Mississippi watersheds of BMU 3. Wells and springs having sulfate concentrations greater than 250 mg/L are common in the Eastern Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland watershed in BMU 3, and are very common in the Western Pennyroyal and Western Coal Field Regions of the Green River watershed in BMU 4.

As was the case for conductivity (Fig. 19) and chloride (Fig. 39), a band of high-sulfate values occurs along the Dripping Springs Escarpment separating the Eastern and Western Pennyroyal Regions. Discharge of sulfate-rich, brackish to moderately saline groundwater from beneath the Western Coal Field or the Mammoth Cave Plateau is a likely cause of the observed sulfate values along the Eastern Pennyroyal–Western Pennyroyal boundary.

Groundwater from wells is much more likely to have high sulfate concentrations than groundwater from springs (Fig. 47). This observation has also been reported by Brown and Lambert (1963).

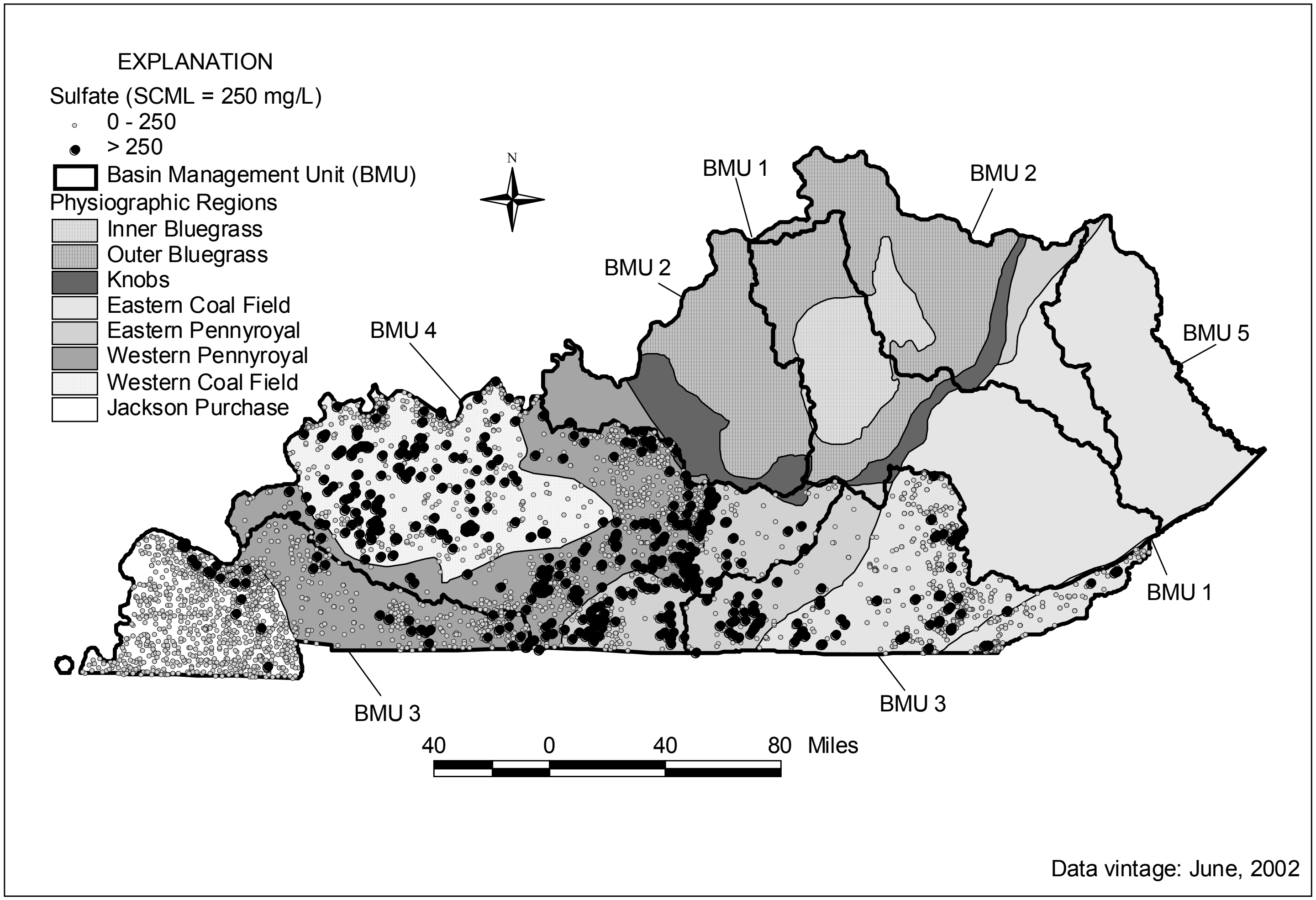


Figure 45. Sample sites and sulfate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

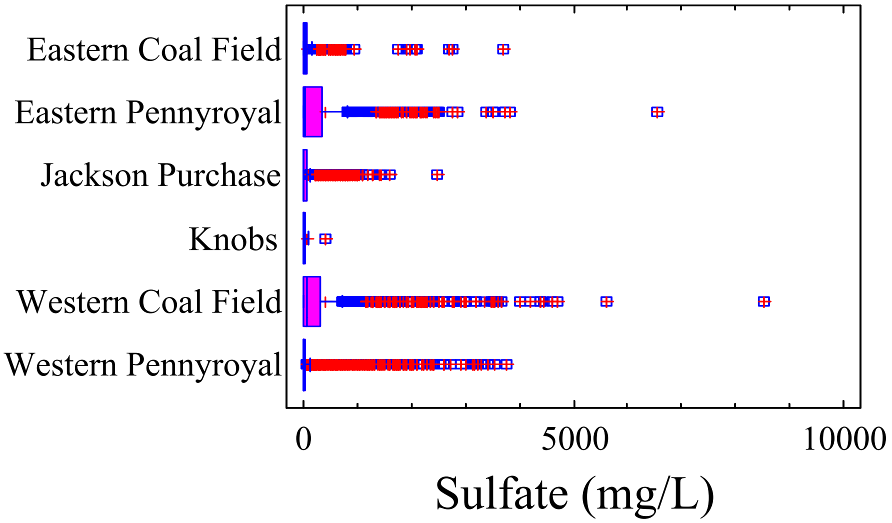


Figure 46. Summary of sulfate concentrations grouped by physiographic region. SMCL = 250 mg/L.

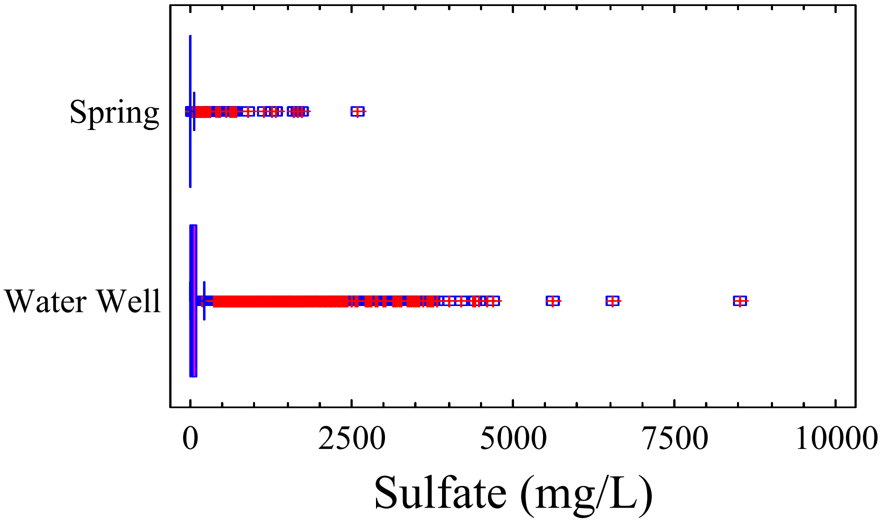


Figure 47. Summary of sulfate concentrations grouped by site type. SMCL = 250 mg/L.

Although there is scatter in the data, sulfate concentrations generally decrease with well depth (Fig. 48).

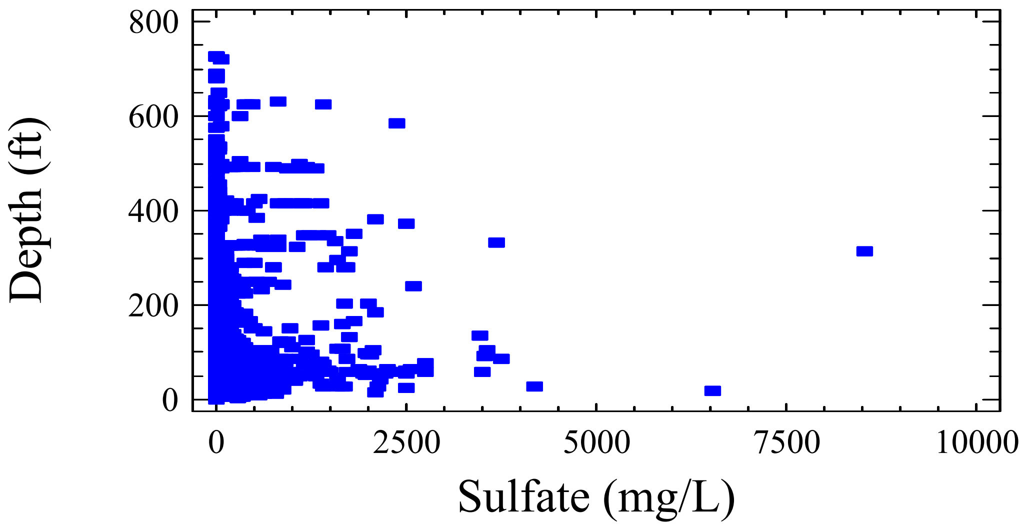


Figure 48. Plot of sulfate values versus well depth. SMCL = 250 mg/L.

Summary: Approximately 95 percent of the reported sulfate concentrations in BMU 3 and 80 percent of the values in BMU 4 are less than the SMCL of 250 mg/L. Sites in BMU 4 have more high sulfate concentrations (> 1,000 mg/L) than sites in BMU 3. The observation that high sulfate concentrations show the same geographic distribution as the very high conductance and chloride values discussed previously suggests that some wells and springs may be contaminated by saline brines from oil and gas wells. Natural oxidation of pyrite is undoubtedly the cause of high sulfate concentrations at some sites in the Eastern and Western Coal Fields.

Fluoride

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

Because of the proven value of fluoride in maintaining healthy teeth and bones, fluoride is added to public water supplies in Kentucky. The concentration in public water is approximately 1 mg/L. Although fluoride has a beneficial effect within a range of low concentrations, at higher concentrations it may cause pain and weakness of the bones, and staining or mottling of teeth. The U.S. Environmental Protection Agency has established a maximum contaminant level (MCL) for fluoride in public drinking water of 4 mg/L.

Fluoride in Kentucky groundwater has been measured in 11,611 samples from 5,751 sites, with median values of 0.10 and 0.17 mg/L in BMU 3 and BMU 4, respectively (Table 12). Fluoride concentrations greater than 4 mg/L are not restricted to any depth range. More than 99 percent of all measurements are less than the 4.0 mg/L MCL (Table 11).

Table 12. Summary of fluoride measurements (mg/L).

Parameter	BMU 3	BMU 4
Measurements	5,069	6,542
Sites	2,585	3,166
Maximum	78	19
3rd quartile	0.20	0.40
Median	0.10	0.17
1st quartile	0.10	0.10
Minimum	0.00	0.00
% values < 4.0	99.0	99.4
Interquartile range	0.10 to 0.20	0.10 to 0.40

MCL = 4.0 mg/L

The distribution of reported fluoride concentrations is similar between BMU's 3 and 4 (Fig. 49 and 50).

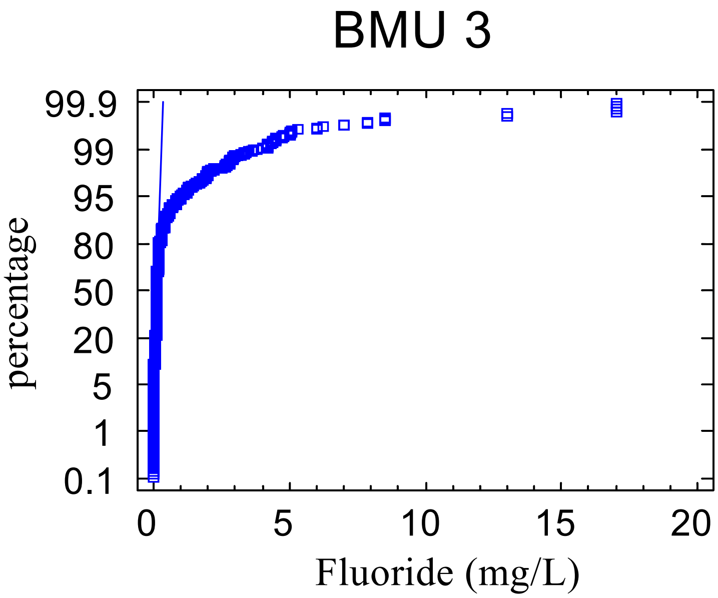


Figure 49. Cumulative plot of fluoride values in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. MCL = 4.0 mg/L.

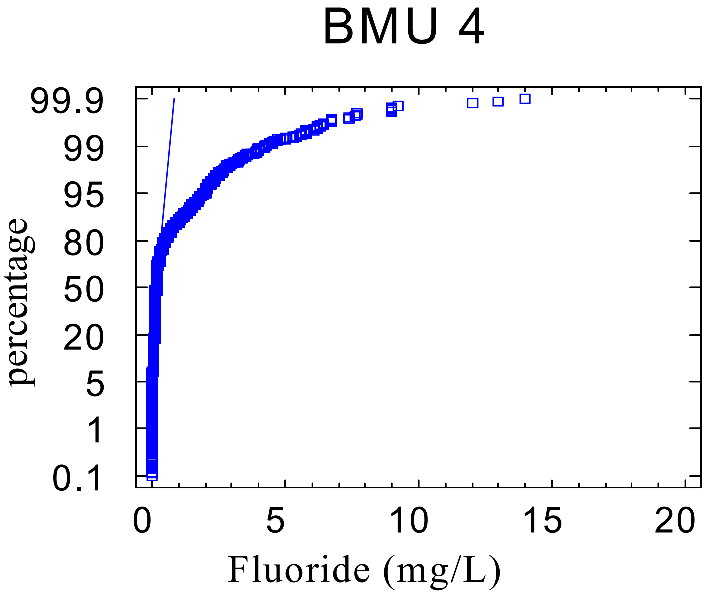


Figure 50. Cumulative plot of fluoride values in BMU 4. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. MCL = 4.0 mg/L.

Fluoride concentrations greater than 4 mg/L are common in groundwater from the Upper Cumberland, Lower Cumberland, Green, and Tradewater River watersheds, but rare in the Tennessee and Mississippi River watersheds (Fig. 51).

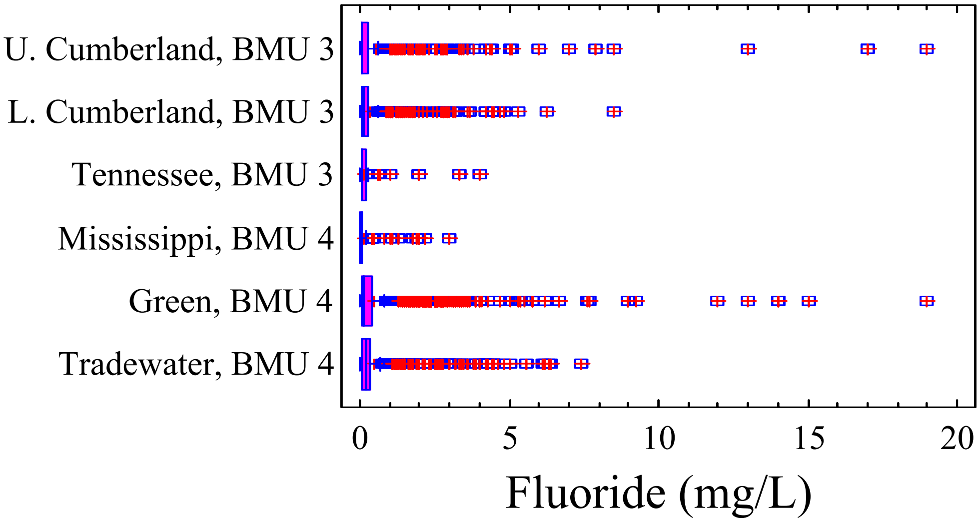


Figure 51. Summary of fluoride measurements grouped by major watershed. One extreme value of 78 mg/L is probably erroneous and was omitted so the majority of the data could be shown more clearly. MCL = 4.0 mg/L.

The map (Fig. 52) also shows that fluoride values that exceed 4 mg/L are found in the Upper and Lower Cumberland, Green, and Tradewater River watersheds. No sites in the Tennessee River watershed or the Jackson Purchase exceed 4 mg/L.

Grouping the data by underlying lithology (Fig. 53) shows that high fluoride values are typical in both Eastern and Western Coal Fields and both Eastern and Western Pennyroyal Regions. Fluoride concentrations are generally lower in the siliciclastic Knobs Region and the Jackson Purchase.

More fluoride concentrations that are greater than 4 mg/L are reported in groundwater from wells than from springs (Fig. 54). The majority of the fluoride data show a general decrease in concentration with well depth (Fig. 55).

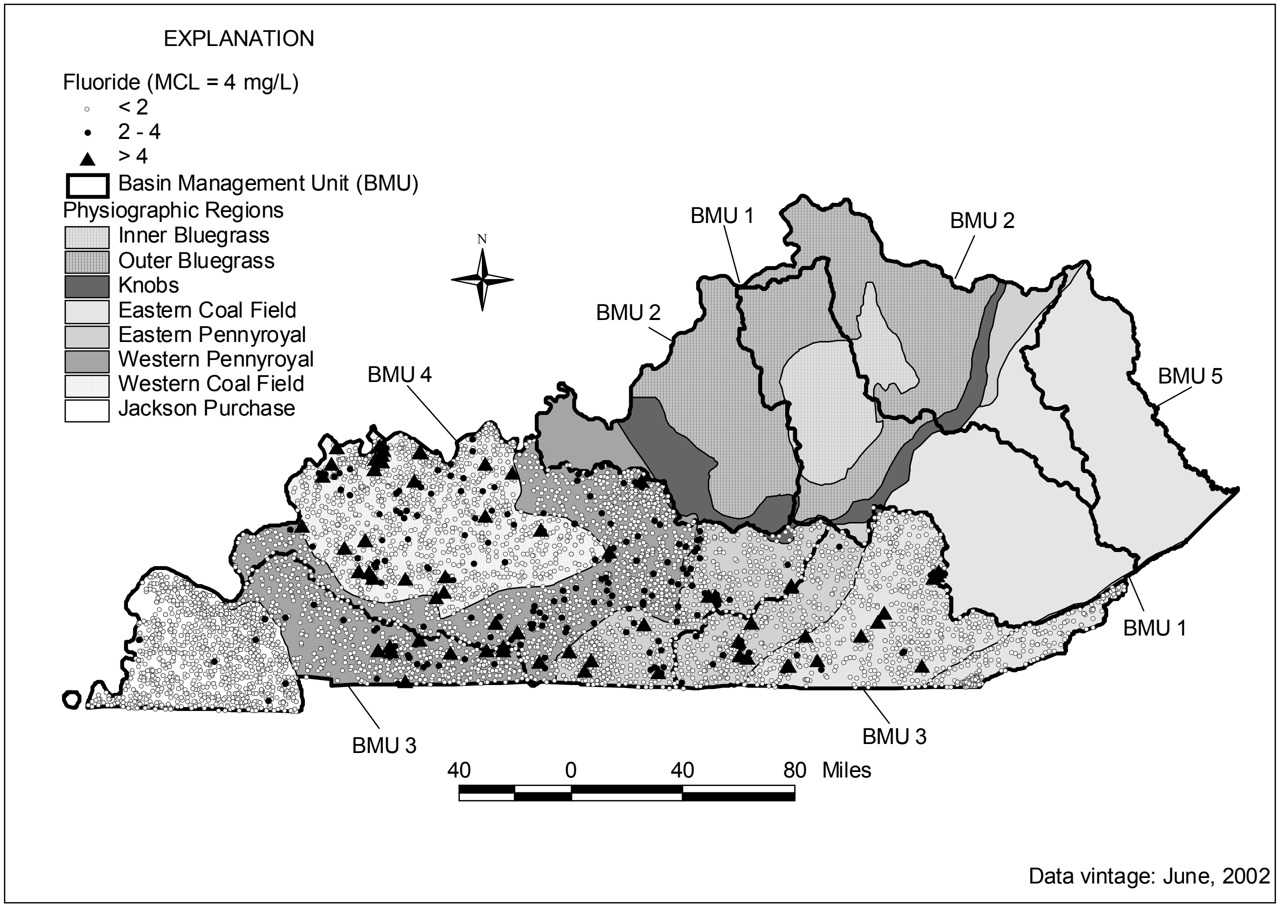


Figure 52. Sample sites and fluoride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

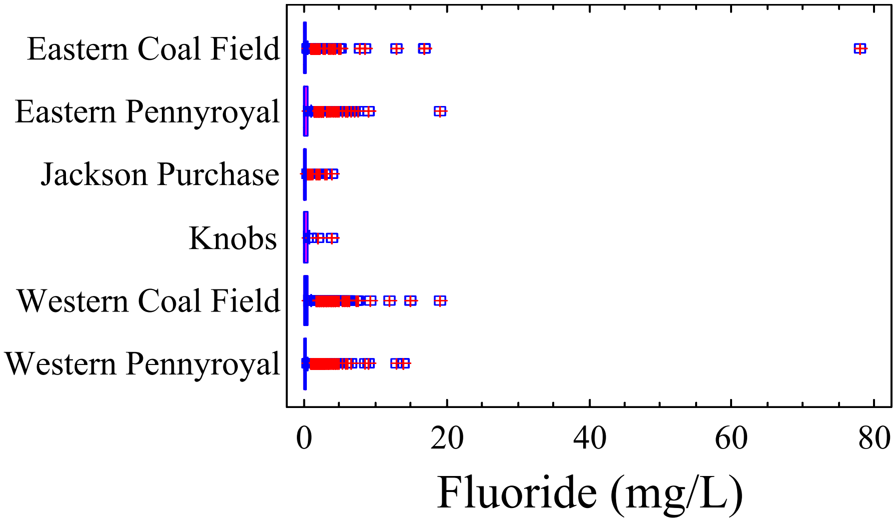


Figure 53. Summary of fluoride values grouped by physiographic province. MCL = 4.0 mg/L.

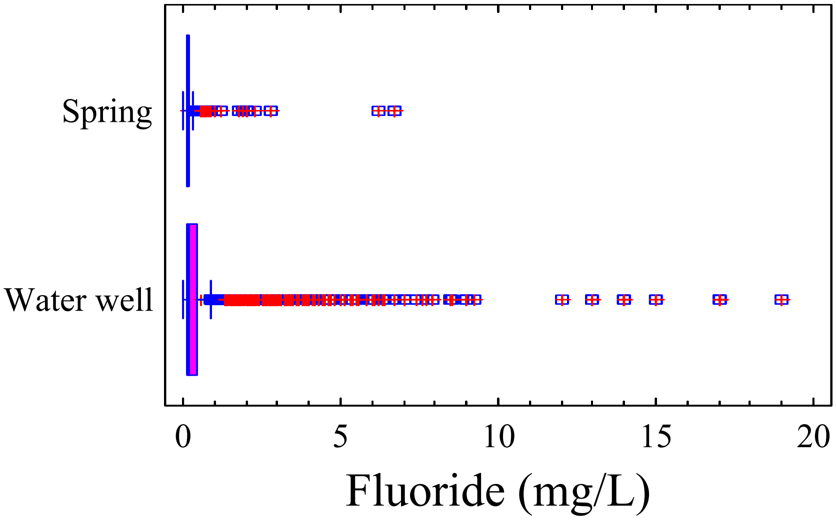


Figure 54. Summary of fluoride measurements grouped by site type. One extreme value of 78 mg/L is probably erroneous and was omitted so the majority of the data could be shown more clearly. MCL = 4.0 mg/L.

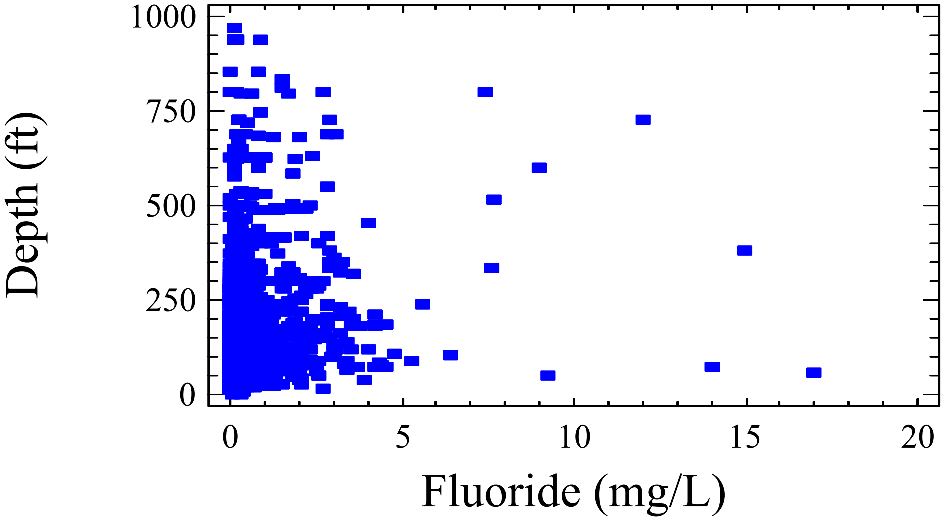


Figure 55. Plot of fluoride values versus well depth. One extreme value of 78 mg/L is probably erroneous and was omitted so the majority of the data could be shown more clearly. MCL = 4.0 mg/L

Summary: The fluoride concentration of ambient groundwater samples in basin management units 3 and 4 is primarily controlled by bedrock lithology. Fewer than 1 percent of all reported analyses exceed the EPA MCL of 4.0 mg/L. There are no obvious nonpoint-source contributions of fluoride to groundwater in the project area.

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

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). Because of these health effects, the U.S. Environmental Protection Agency (EPA) set the maximum contaminant level (MCL) for arsenic in drinking water at 50 parts per billion (ppb, or 0.050 mg/L) in 1974. In 2001 the EPA announced that this MCL will be lowered to 10 ppb (0.010 mg/L). Water-supply systems must meet the new MCL beginning January 2006.

The data repository contained 2,921 measurements of both total and dissolved arsenic in BMU's 3 and 4. These analyses were performed with a variety of analytical 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 (Table 13). Because the new MCL is 0.010 mg/L, measurements reported only as below a detection limit, where the detection limit is 0.010 or greater, provide no useful information. Therefore, measurements reported as less than a detection limit, where the detection limit is 0.010 mg/L or higher, are not included in the following discussion. Removing these values leaves a total of 2,592 arsenic concentrations measured at 501 sites (Table 13). Approximately 86 percent of the arsenic results from BMU 3 were reported as less than the analytical detection limit; approximately 52 percent of the concentrations from BMU 4 were reported as less than the analytical detection limit. Only about 10 percent of the sites (24 of 250 in BMU 3 and 25 of 251 in BMU 4) have reported arsenic concentrations greater than 0.010 mg/L.

Table 13. Summary of arsenic measurements (mg/L).

	BMU 3	**BMU 4**
Measurements	1,086	1,506
Maximum	0.219	0.219
3rd quartile	< 0.002	< 0.002
Median	< 0.002	< 0.002
1st quartile	< 0.002	< 0.002
Minimum	0.001	0.001
Measured values > 0.010 mg/L	49	149
Sites	250	251
Sites with measured values > 0.010 mg/L	24	25

MCL = 0.010 mg/L

Cumulative data plots (Figs. 56 and 57) show a somewhat similar distribution in BMU's 3 and 4, and that there are more measurements greater than the MCL value (0.010 mg/L) in BMU 4 than in BMU 3.

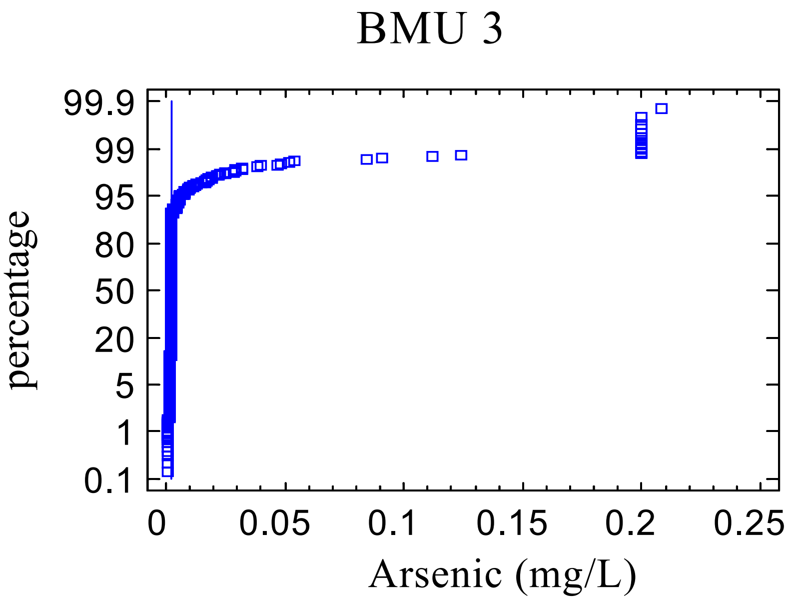


Figure 56. Cumulative plot of arsenic values in BMU 3. Higher values were excluded to show measurements in the range of the MCL (0.010 mg/L).

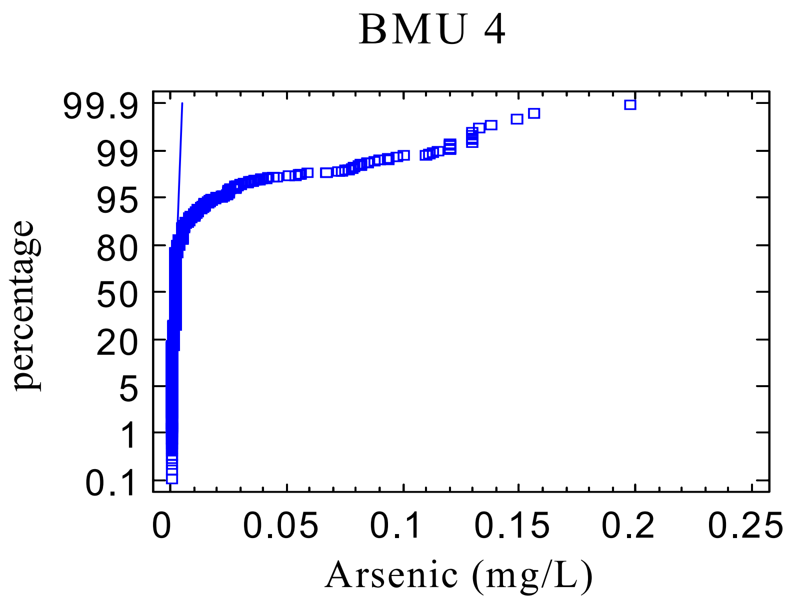


Figure 57. Cumulative plot of arsenic values in BMU 4. Higher values were excluded to show measurements in the range of the MCL (0.010 mg/L).

All major watersheds except the Lower Cumberland River Basin of BMU 3 contain sites where arsenic concentrations exceed the MCL value of 0.010 mg/L (Fig. 58).

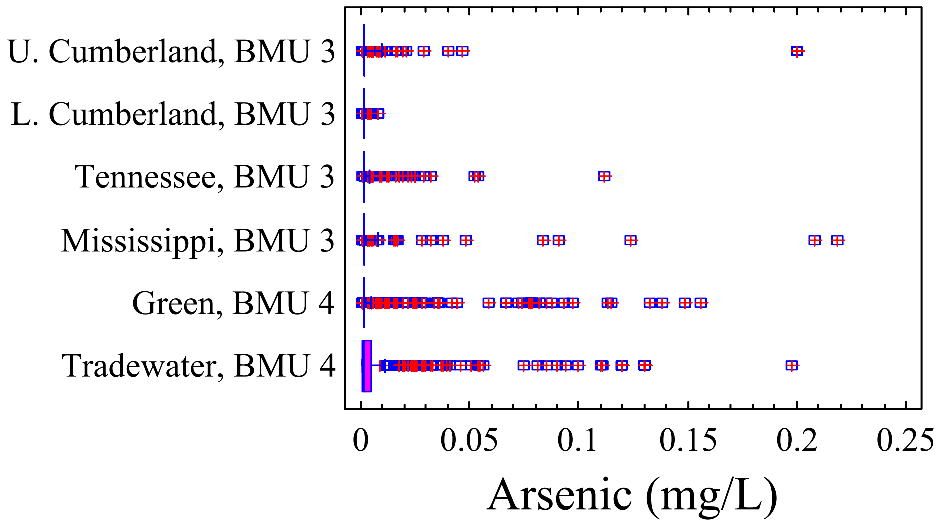


Figure 58. Arsenic results grouped by major watershed. MCL = 0.010 mg/L.

A map (Fig. 59) shows the locations of sampled sites and sites where concentrations exceeded the 0.010 mg/L MCL. Arsenic data are sparse in many regions, and high arsenic concentrations do not occur preferentially in any particular BMU, watershed, or physiographic region. The greatest number of high arsenic concentrations were found at sites in the Green and Tradewater River Basins (BMU 4: Figs. 58 and 59). In BMU 3, high arsenic concentrations were found in watersheds of the Upper Cumberland, Tennessee, and Mississippi Rivers; groundwater from the Lower Cumberland River Basin had relatively low arsenic concentrations (Figs. 58 and 59). Arsenic concentrations exceed the MCL in all physiographic regions (Fig. 60)

Dissolved arsenic concentrations measure a filtered sample, and total arsenic concentrations measure an unfiltered sample. Because many wells are not cased throughout their length, well purging methods can stir up sediment, and arsenic that is adsorbed onto the sediment would be analyzed as part of the total sample. It is possible that total arsenic concentrations would be systematically higher than dissolved arsenic concentrations in this case. Figure 61 shows that total arsenic concentrations range to higher values than dissolved arsenic concentrations, although there is considerable overlap of the values. Arsenic associated with suspended solids would be less mobile than arsenic in true solution in the groundwater. Therefore, if an individual site showed a high total arsenic (or other metal) concentration but low dissolved arsenic concentration, the arsenic is probably not mobile in a porous-media groundwater system. However, if total and dissolved arsenic concentrations are comparable, the arsenic (or other metal) is probably in true aqueous solution and therefore mobile in the groundwater system.

Samples from wells have more instances of high arsenic values than samples from springs (Fig. 62), and relatively shallow wells (30 to 80 feet deep) generally have the highest arsenic concentrations (Fig. 63).

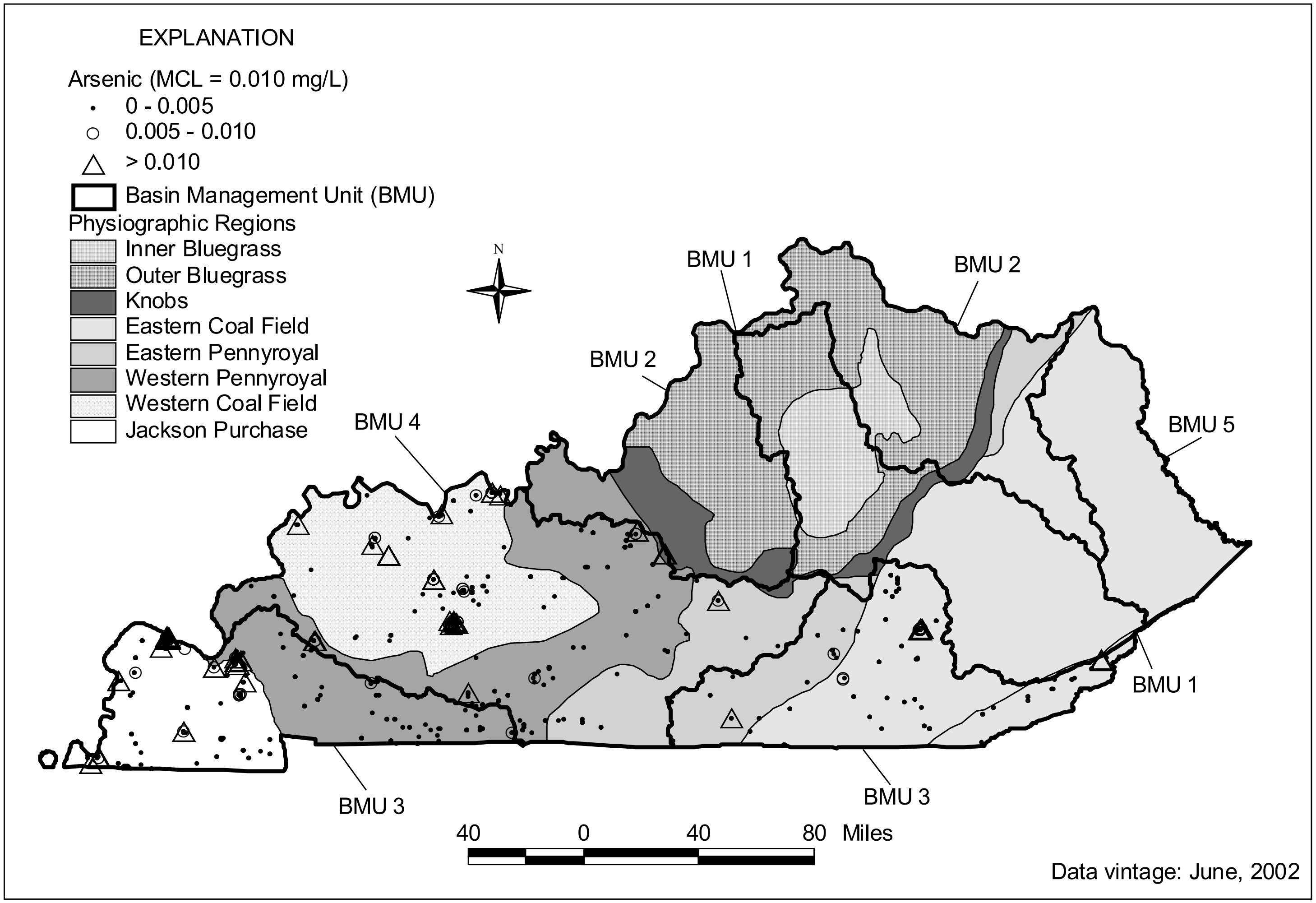


Figure 59. Sample sites and arsenic values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

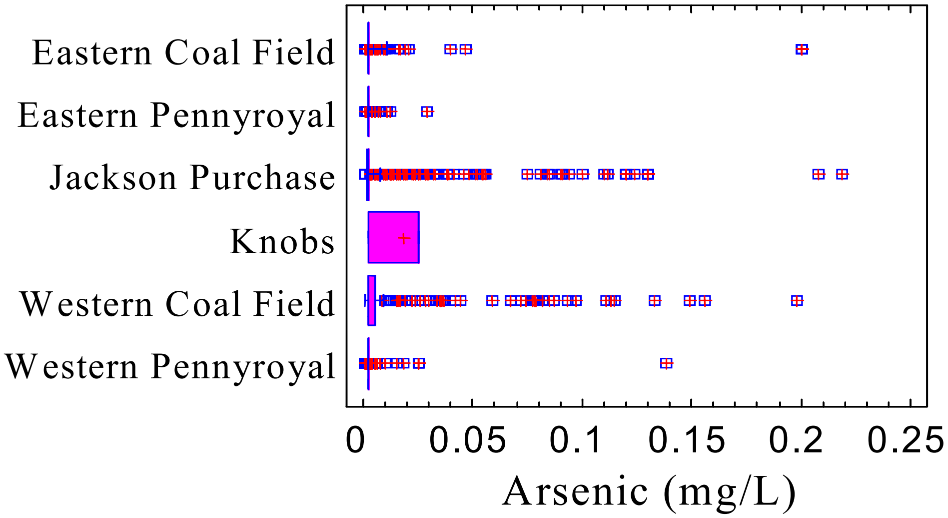


Figure 60. Summary of arsenic concentrations grouped by physiographic region. MCL = 0.010 mg/L.

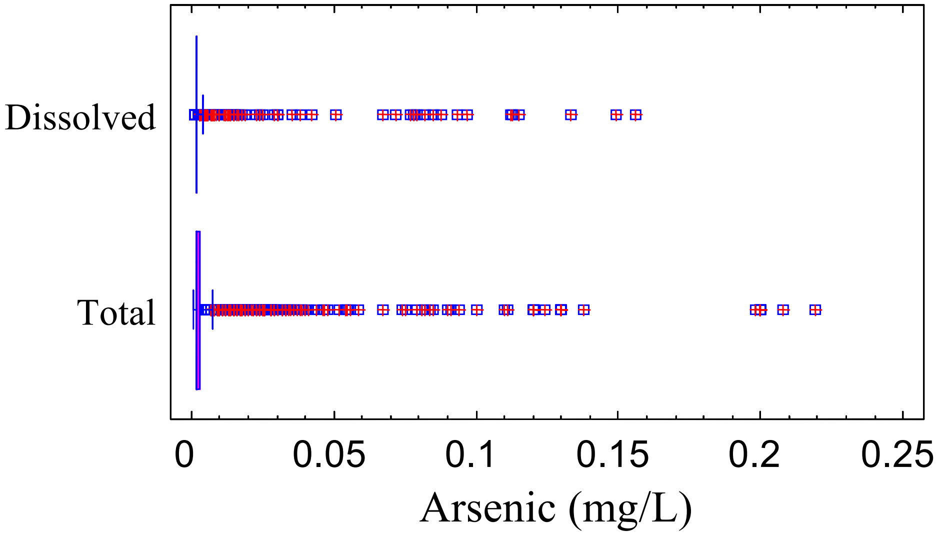


Figure 61. Comparison of total and dissolved arsenic concentrations. MCL = 0.010 mg/L.

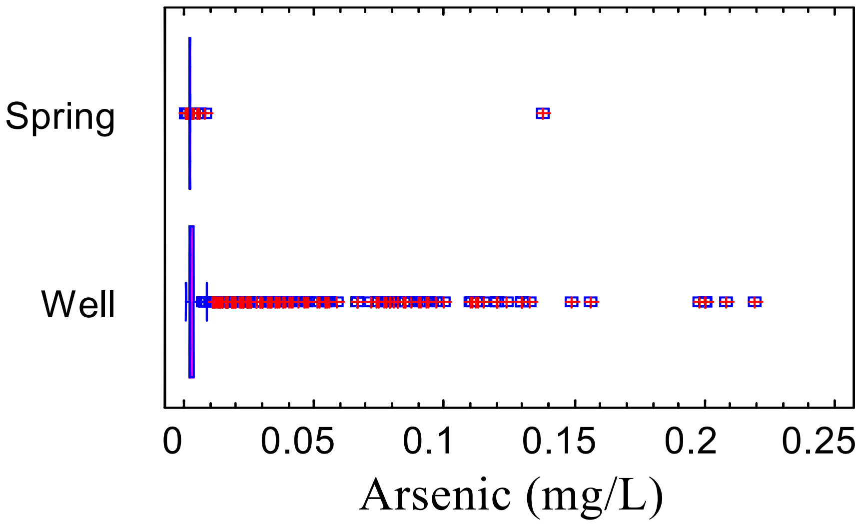


Figure 62. Comparison of arsenic concentrations from wells and springs. MCL = 0.010 mg/L.

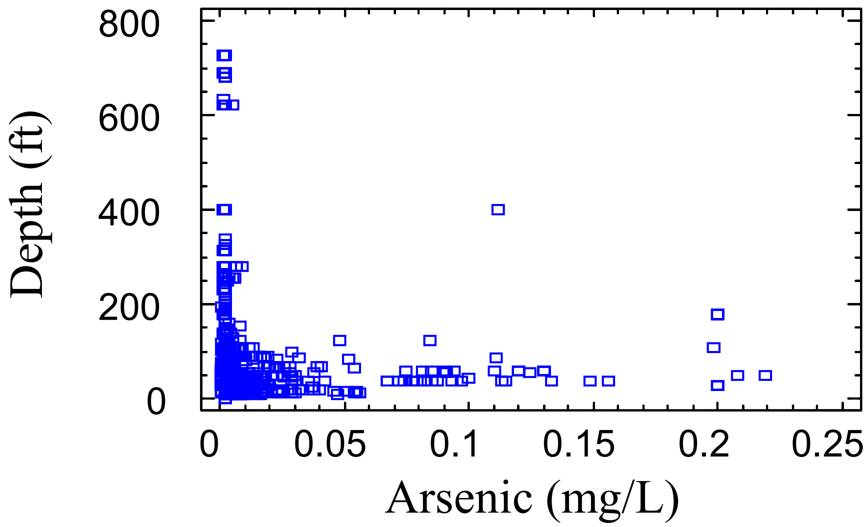


Figure 63. Plot of arsenic concentration versus well depth. MCL = 0.010 mg/L.

Summary: Most arsenic measurements in groundwater are below the MCL value, and most wells and springs in the project area produce water with arsenic levels below the MCL. However, groundwater having an arsenic concentration that exceeds the MCL exists in both BMU's 3 and 4, in every physiographic region in the project area, and in every major watershed except the Lower Cumberland. Sites where arsenic concentrations exceed the MCL are most common in the Western Coal Field and the Jackson Purchase. Arsenic concentrations are generally higher in unfiltered water samples rather 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 feet 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 well bore than in the regional groundwater system. A statewide summary of arsenic data is available (Fisher, 2002a) and can be viewed on the KGS 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's 3 and 4 are generally well below levels of concern. The data repository contained 2,895 barium measurements, with only one value greater than the MCL of 2.0 mg/L (Table 14). That sample was collected in 1998 from a 108-foot-deep well in the Western Coal Field. With this one exception, barium in groundwater is less than 2.0 mg/L in the project area.

Table 14. Summary of barium measurements (mg/L).

	BMU 3	**BMU 4**
Measurements	1,237	1,658
Sites	327	288
Maximum	1.200	3.04
3rd quartile	0.057	0.10
Median	0.038	0.041
1st quartile	0.019	0.026
Minimum	< 0.0007	0.000
Interquartile range	0.019 to 0.057	0.026 to 0.100
Measurements > 2.0	0	1
Sites > 2.0	0	1

MCL = 2.0 mg/L

Cumulative data plots (Figs. 64 and 65) show that approximately 99 percent of the measurements in both BMU's are less than 0.5 mg/L. A summary of reported concentrations grouped by major watershed (Fig. 66) shows that barium concentrations greater than 1.0 mg/L (half the MCL) occur in each watershed except that of the Lower Cumberland River.

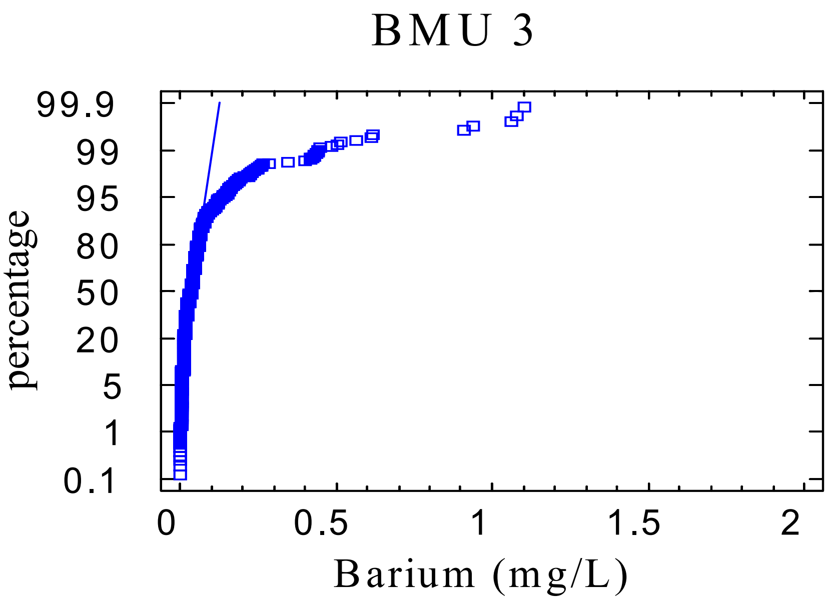


Figure 64. Cumulative plot of barium values in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. MCL = 2.0 mg/L.

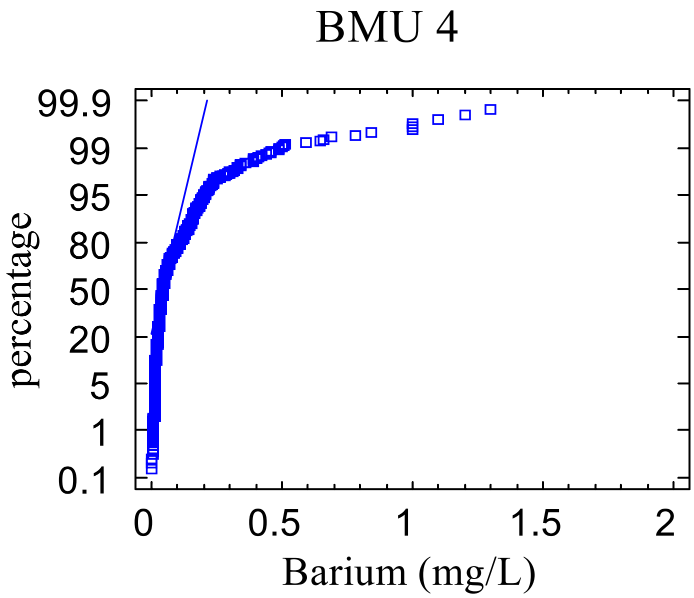


Figure 65. Cumulative plot of barium values in BMU 4. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. MCL = 2.0 mg/L.

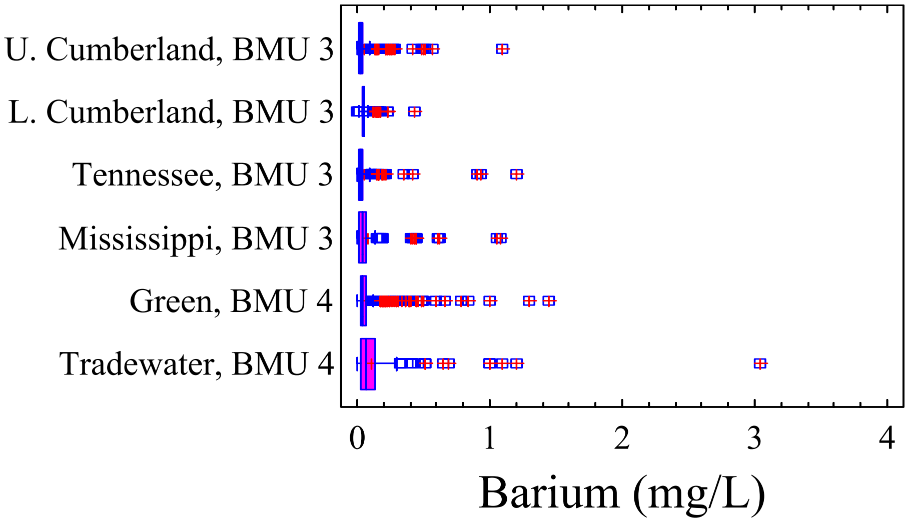


Figure 66. Summary of barium concentrations grouped by major watershed. MCL = 2.0 mg/L.

A map (Fig. 67) and summary of measured values grouped by physiographic region (Fig. 68) show that barium values greater than 1.0 mg/L are uncommon. Isolated sites yielding such groundwater are found in the Eastern and Western Coal Fields, the Western Pennyroyal, and the Jackson Purchase.

Total barium concentrations (unfiltered samples) tend to be higher than dissolved barium concentrations (filtered samples), demonstrating that barium is associated with suspended particulate material (Fig. 69). Groundwater from wells generally has higher barium concentrations than groundwater from springs (Fig. 70). Higher barium concentrations are reported from wells less than 100 feet deep than from deeper wells that sample slower groundwater flow systems (Fig. 71).

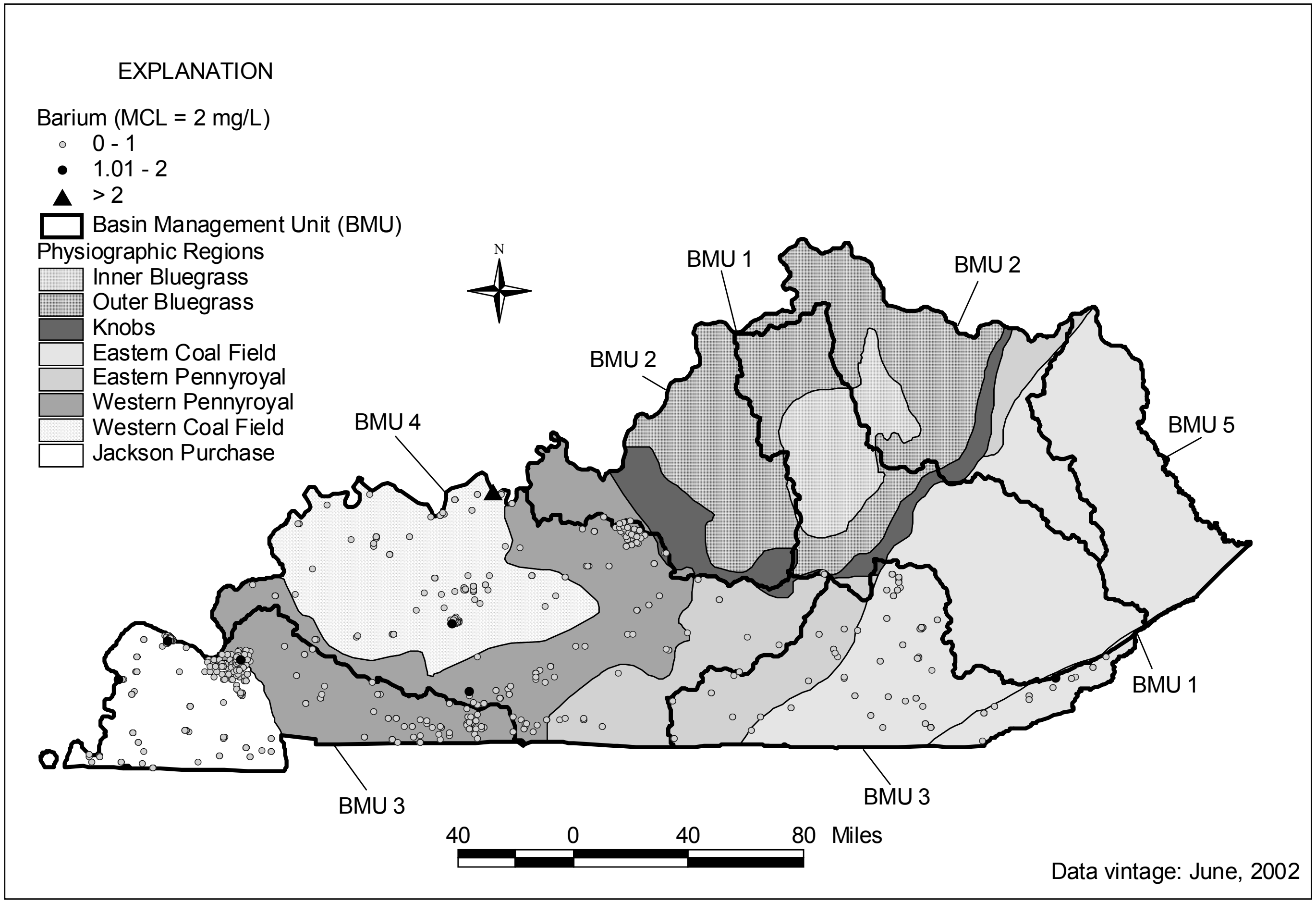


Figure 67. Sample sites and barium values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

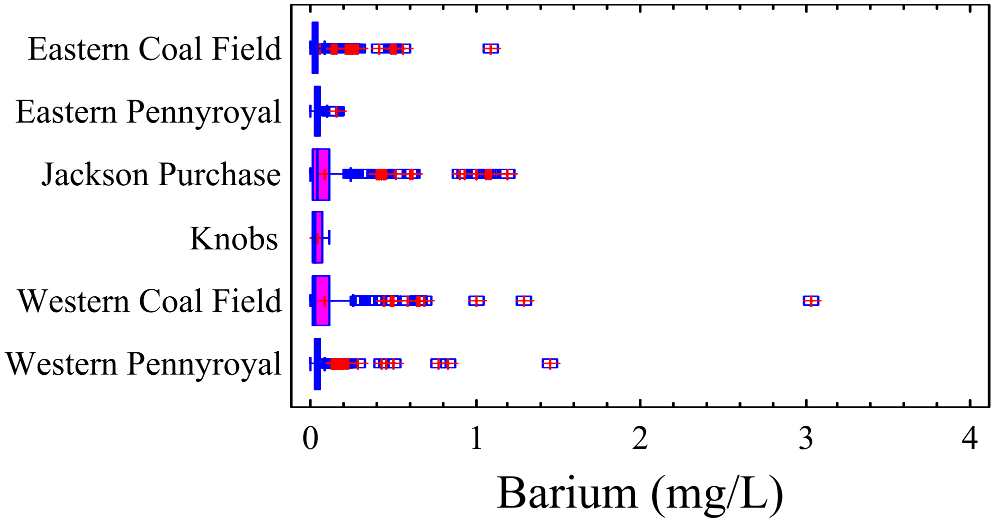


Figure 68. Summary of barium measurements grouped by physiographic region. MCL = 2.0 mg/L.

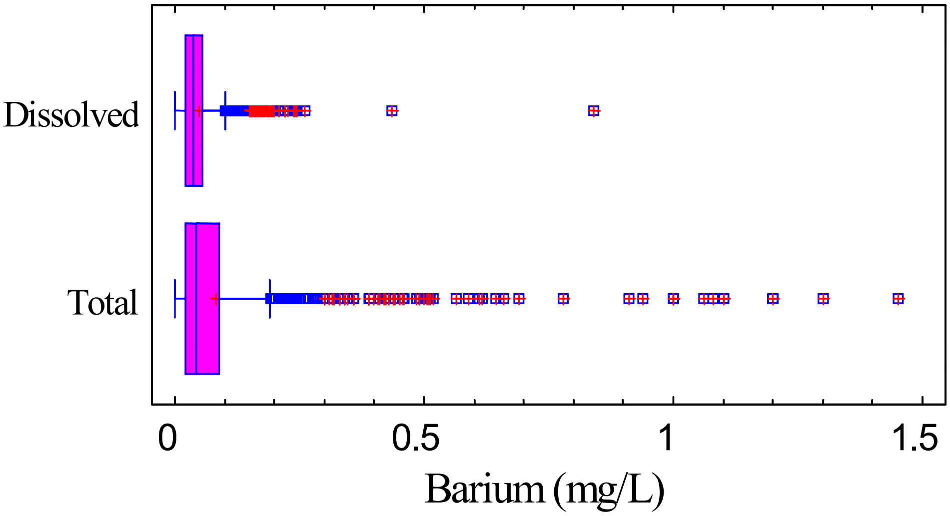


Figure 69 Comparison of total and dissolved barium concentrations. Values greater than 1.5 mg/L were omitted to better show the majority of reported analytical results. MCL = 2.0 mg/L.

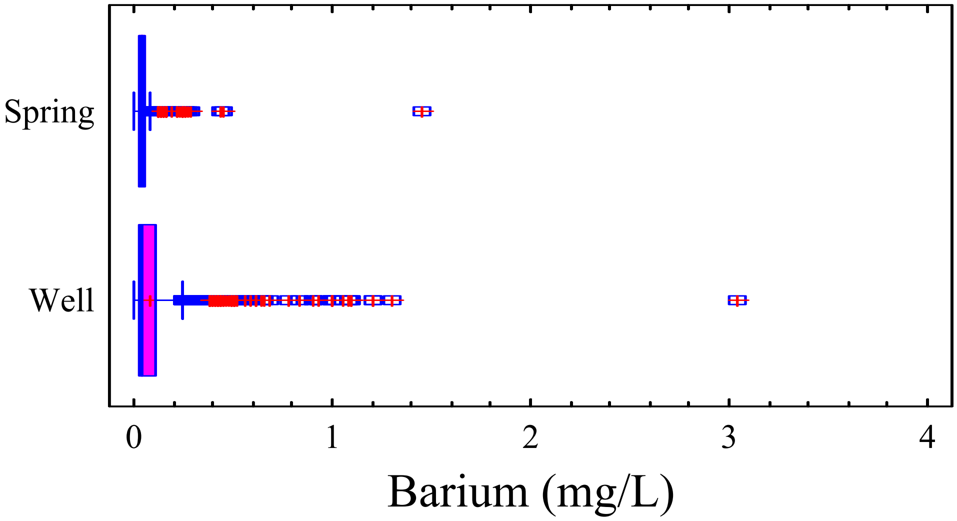


Figure 70. Comparison of barium measurements grouped by site type. MCL = 2.0 mg/L.

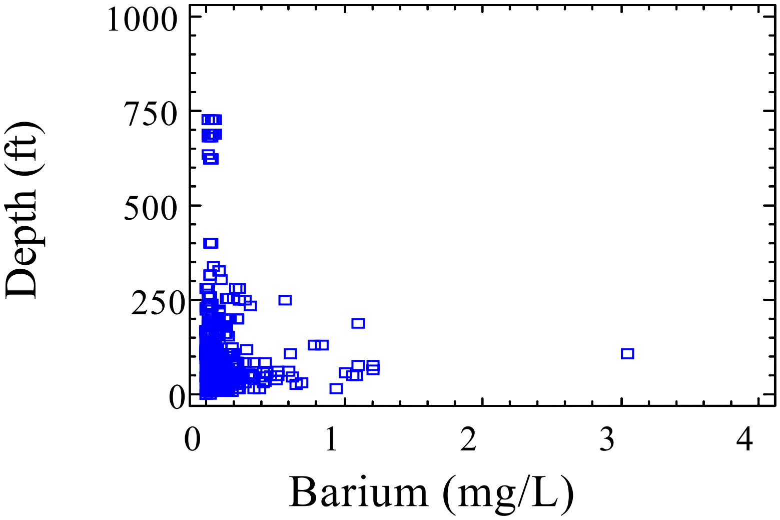


Figure 71. Plot of barium concentrations versus well depth. MCL = 2.0 mg/L.

Summary: Barium concentrations in Kentucky groundwater are generally well below the health-based MCL established by the EPA. Barium concentrations do not appear to be affected by NPS factors, but are more likely the result of natural hydrogeologic processes. Only one reported measurement exceeded the MCL of 2.0 mg/L. There is no clear association of barium concentrations greater than one-half the MCL with physiographic region or major watershed. Groundwater from wells typically has higher barium concentrations than water from springs, and higher barium concentrations are more common in water from shallow wells than from deep wells.

Mercury

Mercury (Hg) is a liquid metal found in natural deposits as ores containing other elements. Forest fires, coal combustion products, disposal of mercury-containing products such as electric lights and switches, computers, and blood-pressure gauges 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 methylmercury, 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 Hg is a strong neurotoxin that causes demyelination, delayed nerve conduction, and kidney damage.

The groundwater data repository contained 1,917 mercury analyses from 441 sites from the project area (Table 15). Approximately 89 percent of the analyses in BMU 3 and 71 percent of the analyses in BMU 4 were reported as less than the analytical detection limit. Only six sites yielded groundwater with mercury concentrations greater than 0.002 mg/L. The median value in both BMU's was reported as less than a detection limit of 0.00005 mg/L.

Table 15. Summary of mercury measurements (mg/L).

	BMU 3	BMU 4
Measurements	940	977
Sites	243	198
Maximum	0.01750	0.00370
3rd quartile	< 0.00005	0.00020
Median	< 0.00005	< 0.00005
1st quartile	< 0.00005	< 0.00005
Minimum	<0.00005	< 0.00004
Measurements > 0.002	25	3
Sites > 0.002	4	2

MCL = 0.002 mg/L

Comparison of the distributions of mercury concentrations (Figs. 72 and 73) shows there are more high values in BMU 3 than in BMU 4. Sites where mercury exceeds the MCL are in the Tennessee River watershed in the Jackson Purchase Region and the Green River watershed in the Western Pennyroyal Region (Figs. 74, 75, and 76).

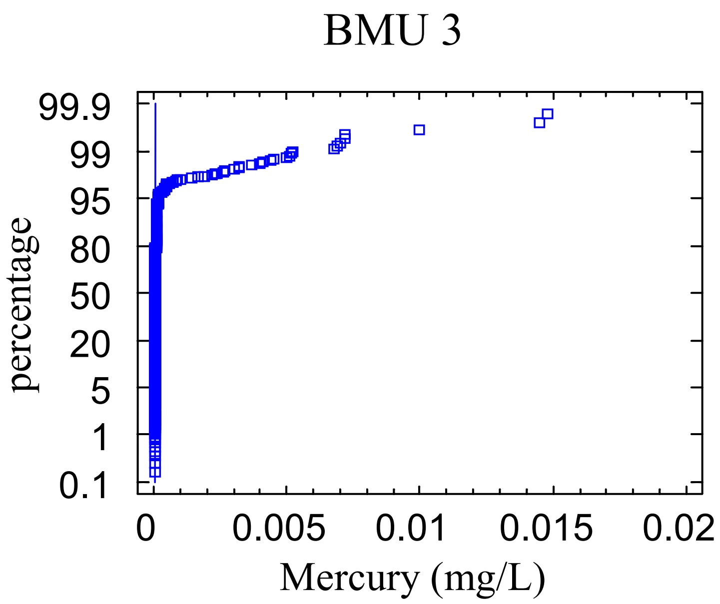


Figure 72. Cumulative plot of mercury values in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. MCL = 0.002 mg/L.

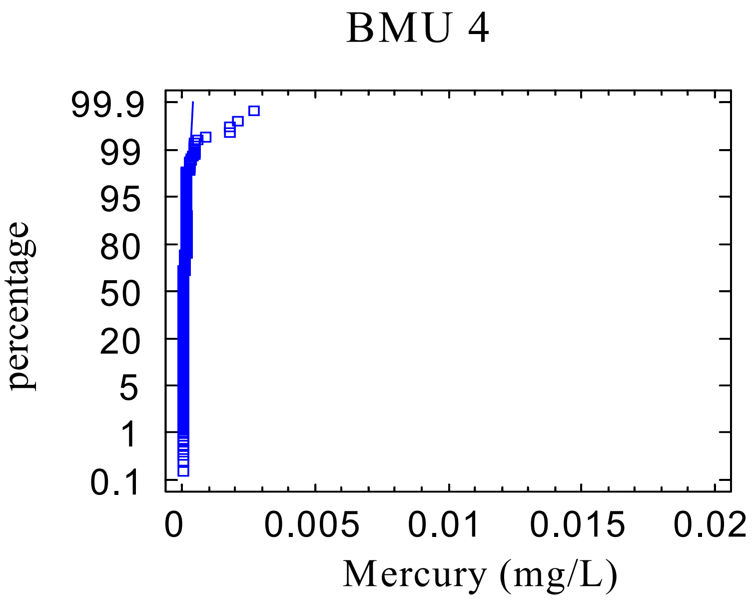


Figure 73. Cumulative plot of mercury values in BMU 4. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. MCL = 0.002 mg/L.

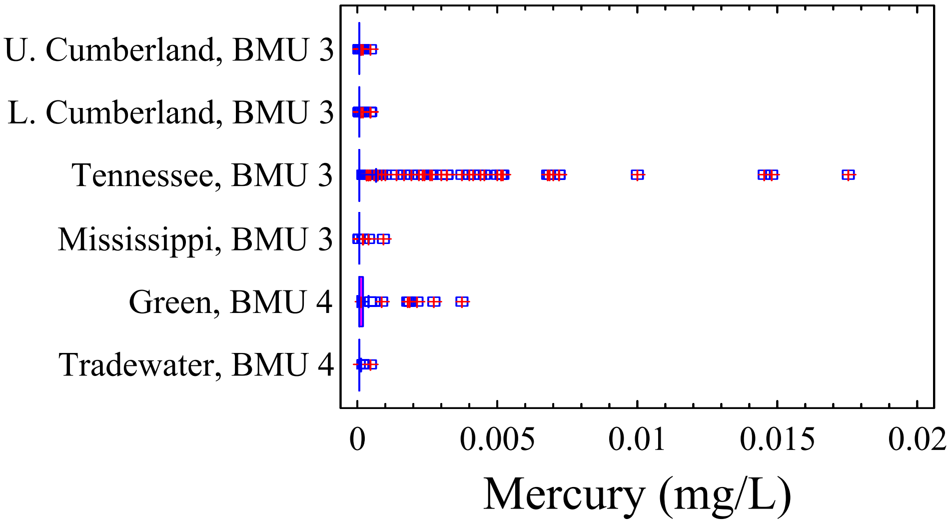


Figure 74. Comparison of mercury values grouped by major watershed. MCL = 0.002 mg/L.

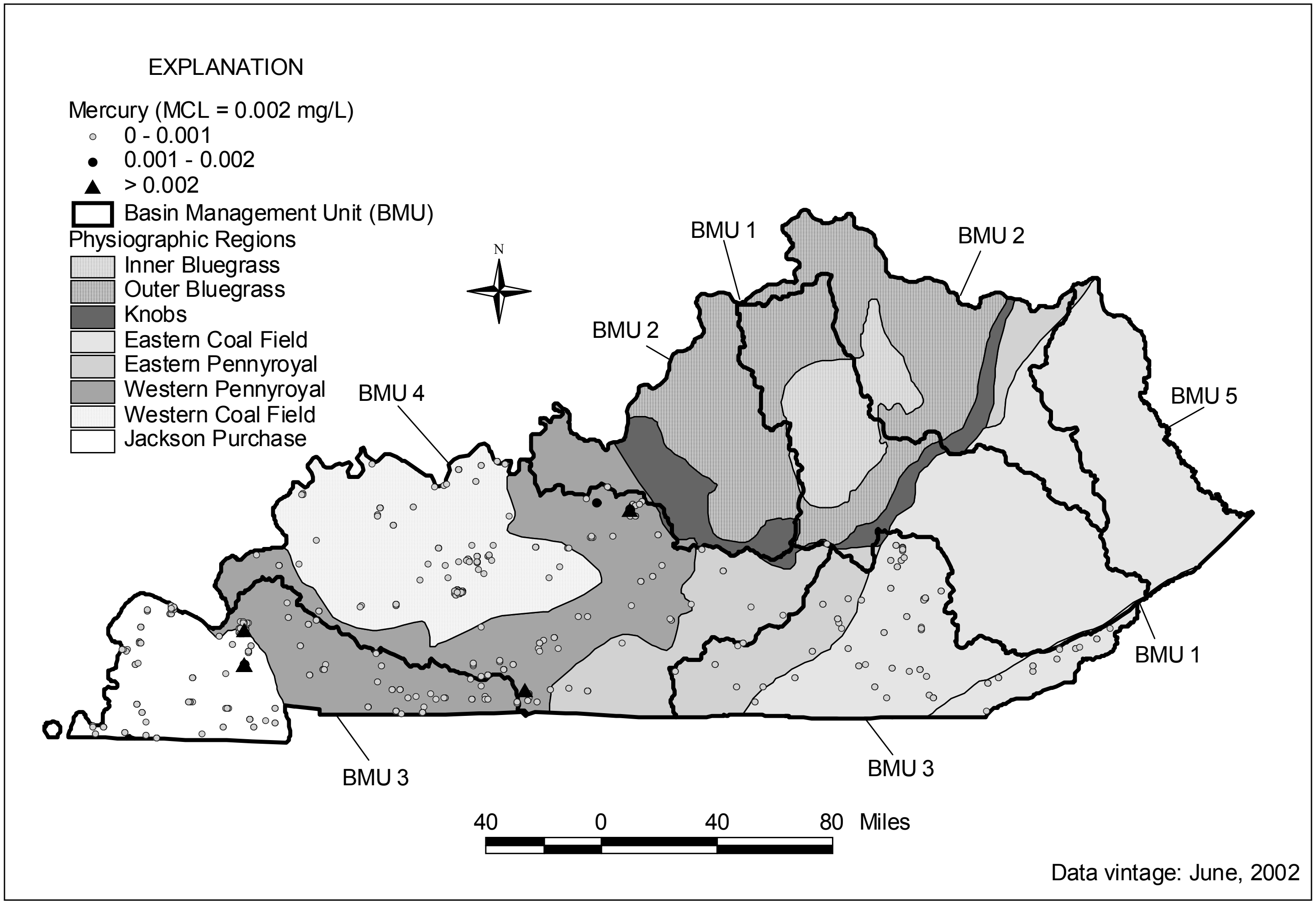


Figure 75. Sample sites and mercury values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

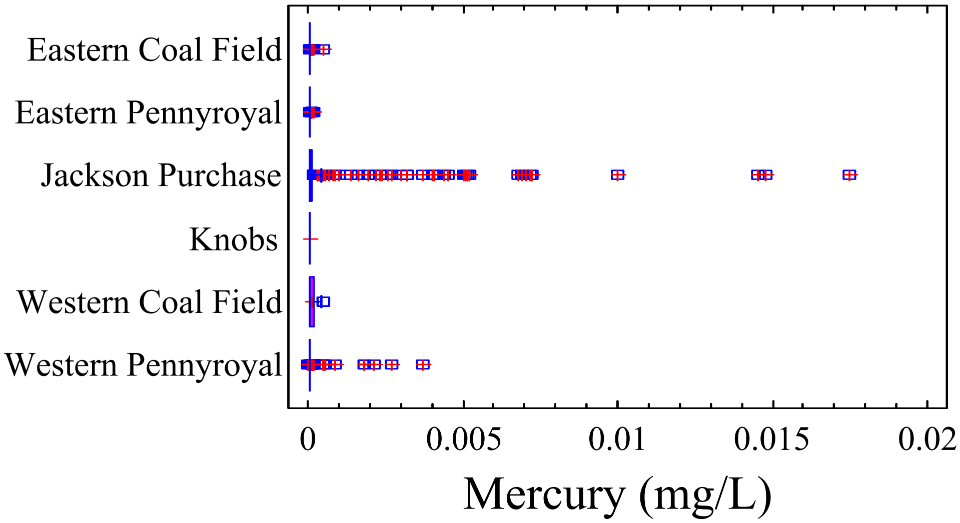


Figure 76. Comparison of mercury values grouped by physiographic region. MCL = 0.002 mg/L.

The highest mercury concentrations are found in unfiltered (total mercury) rather than filtered (dissolved mercury) groundwater (Fig. 77).

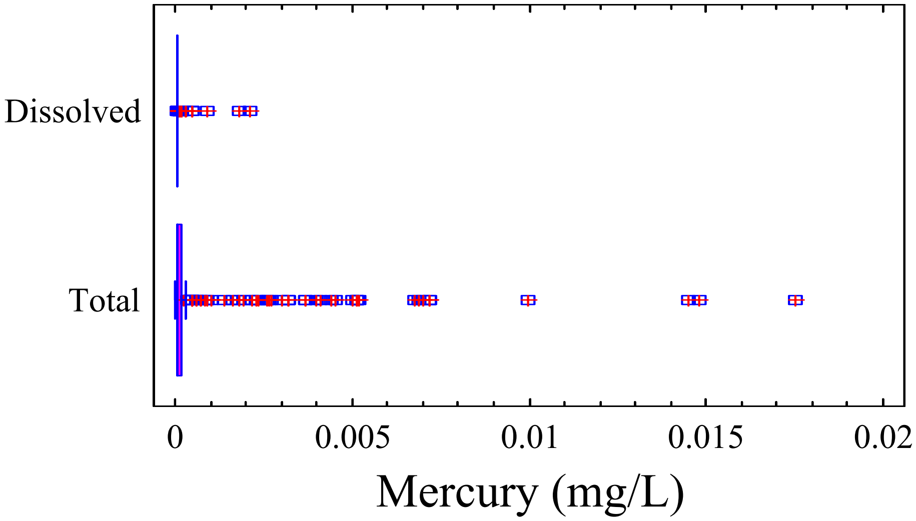


Figure 77. Comparison of dissolved and total mercury concentrations. MCL = 0.002 mg/L.

Wells produce groundwater with higher mercury concentrations than springs (Fig. 78). Shallow wells produce higher mercury concentrations than intermediate or deep wells (Fig. 79).

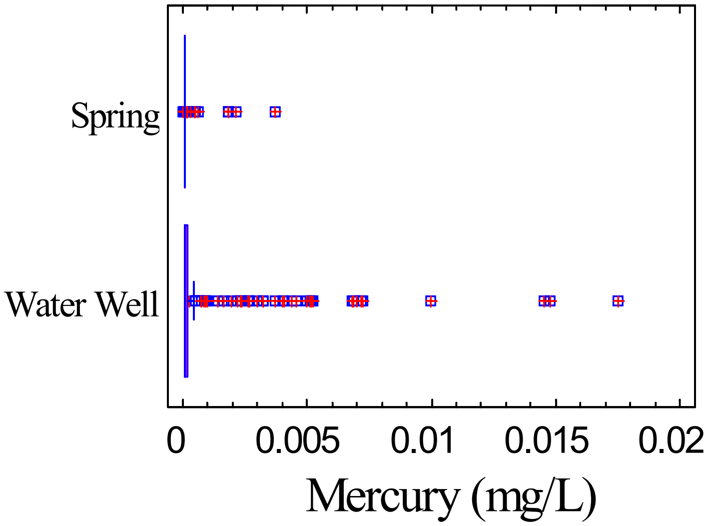


Figure 78. Comparison of mercury values in springs and wells. MCL = 0.002 mg/L.

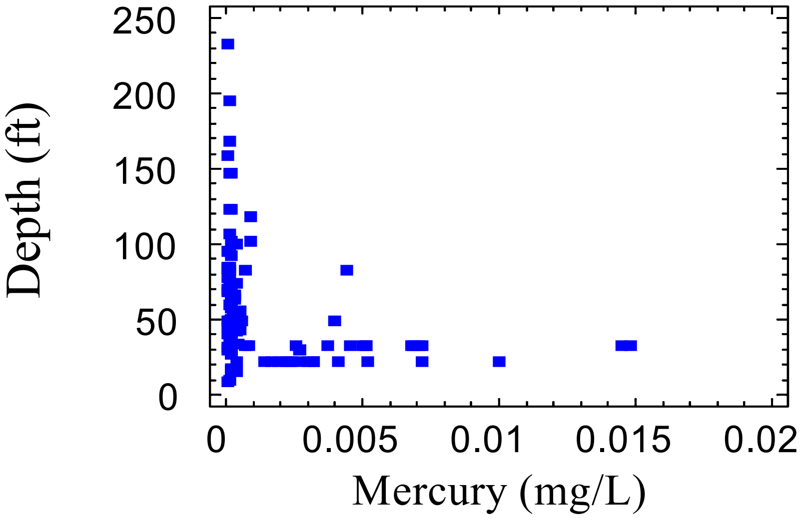


Figure 79. Plot of mercury concentrations versus well depth. Only concentrations reported as above detection limits are shown. MCL = 0.002 mg/L.

Summary: Mercury is rarely present in detectable amounts in groundwater from wells or springs in the project area. There is no evidence of NPS impacts on mercury concentrations in Kentucky groundwater in the project area. Isolated occurrences of mercury concentrations greater than 0.001 mg/L may be natural or may be caused by unrecognized point-source impacts.

Iron

Iron (Fe) is a naturally occurring metal that is widely present in groundwater. Iron can exists 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 poorly crystalline to amorphous material. Under reduced conditions, however, ferrous iron is stable and will remain in groundwater. There is no EPA primary drinking-water standard for iron in water supplies because there are no identified, serious health threats posed by it. There is, however, a secondary standard of 0.3 mg/L for iron because iron concentrations above this level may produce objectionable odor, taste, color, staining, corrosion, and scaling.

The data repository contained 13,126 iron measurements (Table 16) ranging from 7,100 to 0.0 mg/L. In BMU 3 approximately 48 percent (3,462 of 7,242) of the measurements were less than 0.3 mg/L, whereas in BMU 4, approximately 55 percent (3,229 of 5,884) of the measurements were less than 0.3 mg/L. In BMU 3, 43 percent of the sites (852 of 1,963) never produced water with more than 0.3 mg/L iron; in BMU 4 this figure was 45 percent (732 of 1,633).

Table 16. Summary of iron measurements (mg/L).

	BMU 3	**BMU 4**
Measurements	7,242	5,884
Sites	1,963	1,633
Maximum	1,040	7,100
3rd quartile	1.81	1.90
Median	0.34	0.21
1st quartile	0.08	0.04
Minimum	0.00	0.00
Interquartile range	0.08 to 1.81	0.04 to 1.90
Measurements < 0.3 mg/L	3,462	3,229
Sites < 0.3 mg/L	852	732

SMCL = 0.3 mg/L

The distribution of iron concentrations is similar in BMU 3 and BMU 4 (Figs. 80 and 81). However, there are more values greater than 250 mg/L in BMU 4 than in BMU 3.

Iron concentrations greater than 0.3 mg/L occur throughout the project area and are not confined to any physiographic region or watershed (Figures 82, 83, and 84). However, the Lower Cumberland River watershed has lower iron concentrations than any other major watershed in the project area (Fig. 82).

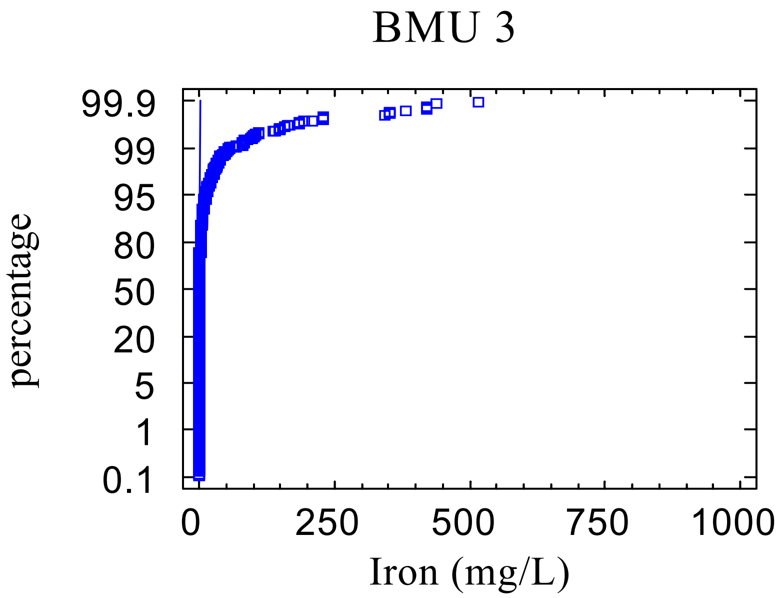


Figure 80. Cumulative plot of iron values in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. SMCL = 0.3 mg/L.

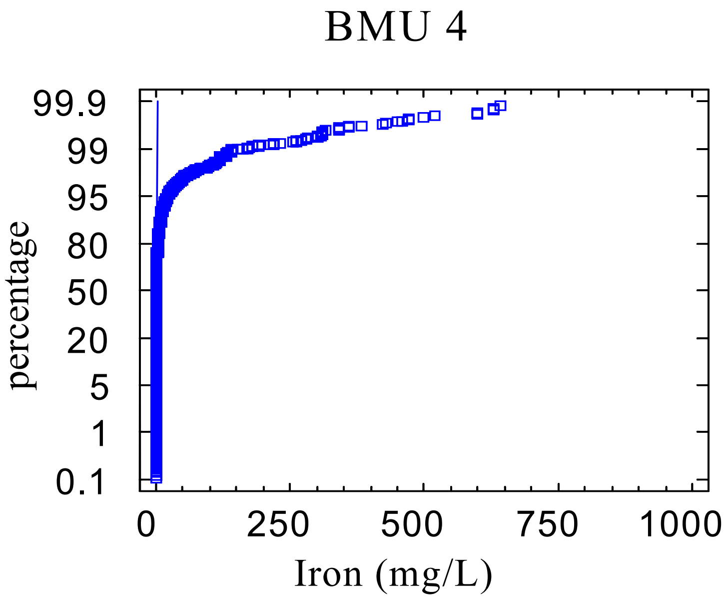


Figure 81. Cumulative plot of iron values in BMU 4. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. SMCL = 0.3 mg/L.

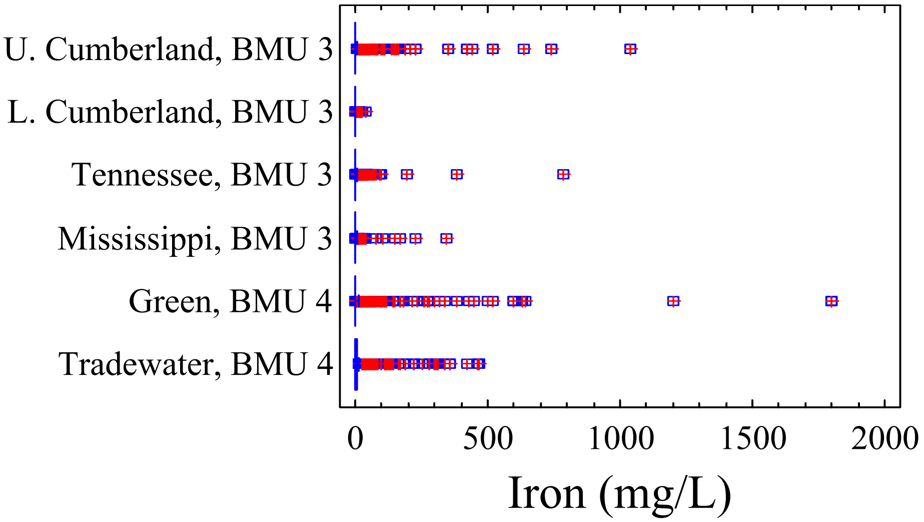


Figure 82. Comparison of iron values grouped by major watershed. Values > 2000 mg/L are omitted to better show the majority of the values. SMCL = 0.3 mg/L.

Total iron concentrations are typically higher than dissolved iron concentrations (Fig. 85). Wells produce groundwater with higher iron concentrations than springs (Fig. 86). This reflects the expected trend of oxidation conditions. Water in springs would be 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. High iron concentrations are more common in wells less than about 100 feet deep than in deeper wells (Fig. 87).

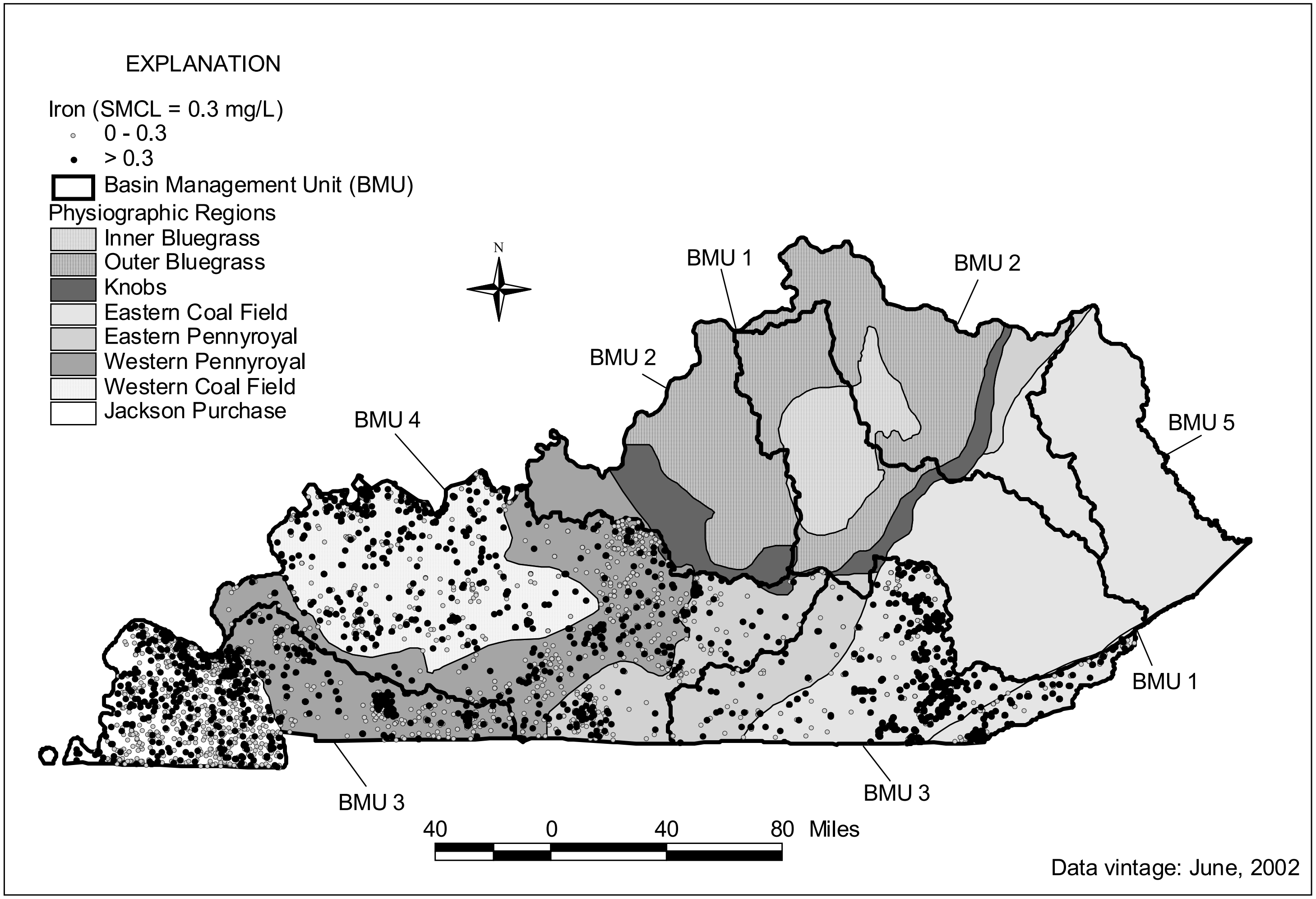


Figure 83. Sample sites and iron concentrations.

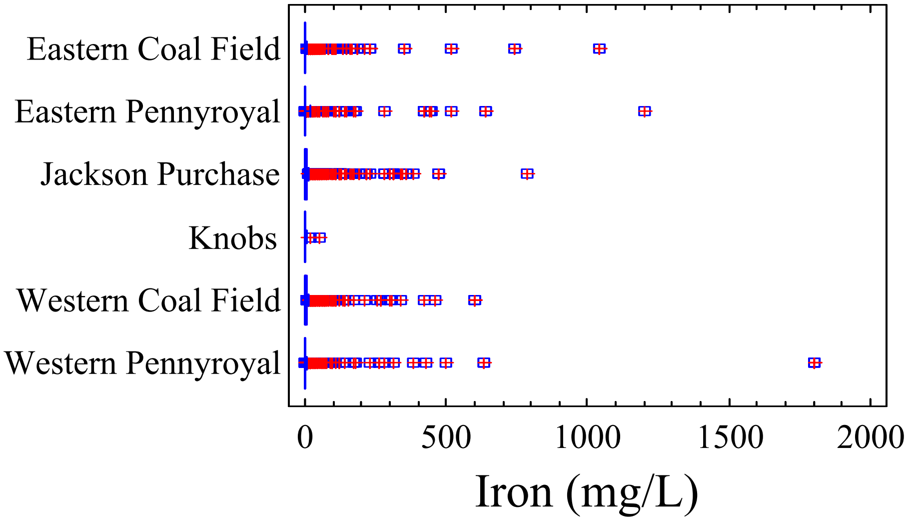


Figure 84. Comparison of iron values grouped by physiographic region. Values > 2,000 mg/L are omitted to better show the majority of the values. SMCL = 0.3 mg/L.

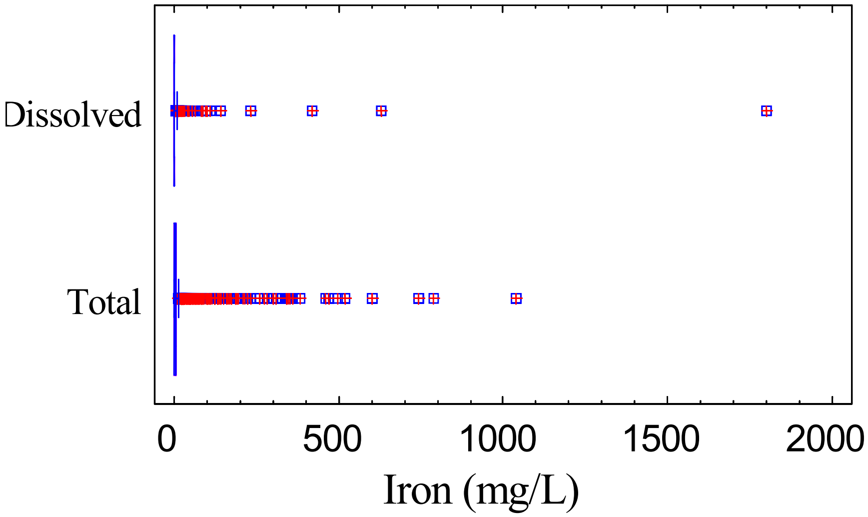


Figure 85. Comparison of total and dissolved iron values. Values > 2,000 mg/L are omitted to better show the majority of the values. SMCL = 0.3 mg/L.

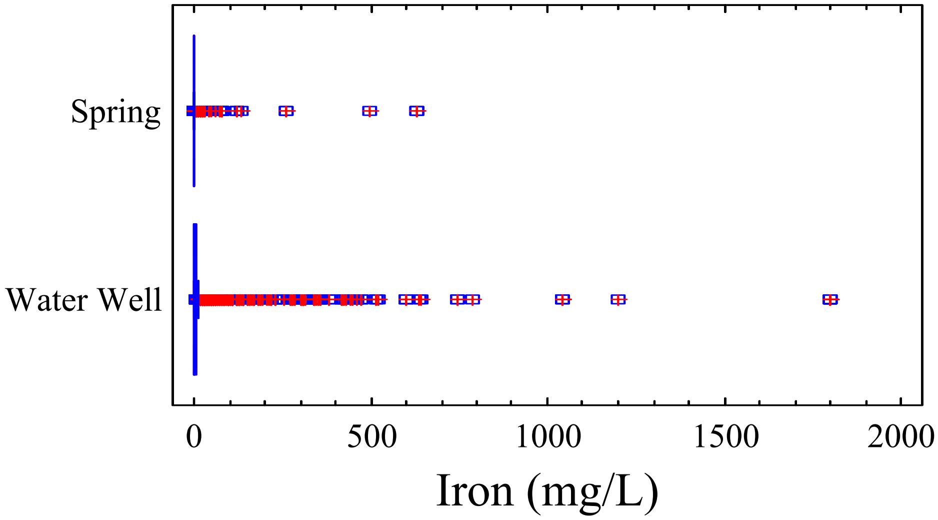


Figure 86. Comparison of iron concentrations by site type. Values > 2,000 mg/L are omitted to better show the majority of the values. SMCL = 0.3 mg/L.

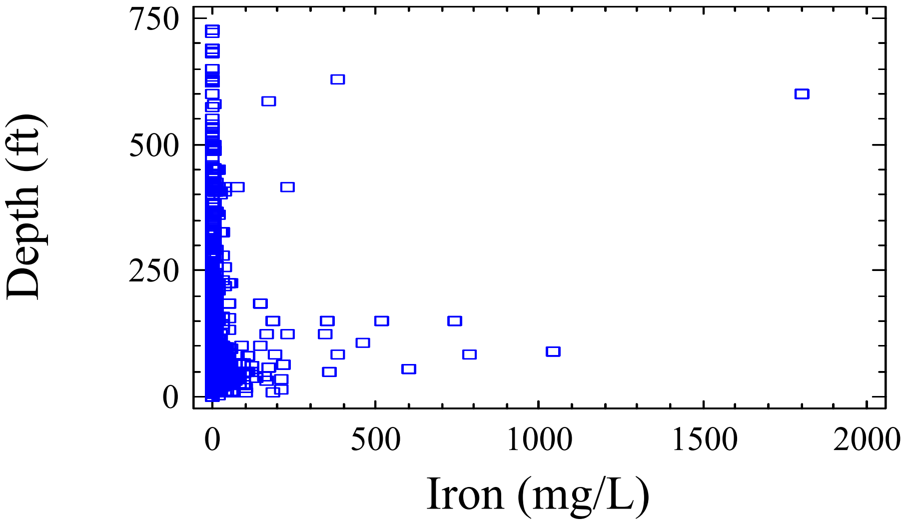


Figure 87. Plot of iron concentrations versus well depth. Values > 2,000 mg/L are omitted to better show the majority of the values. SMCL = 0.3 mg/L

Summary: Approximately half the wells and springs in the project area have never produced groundwater with more than 0.3 mg/L iron. However, many wells and springs that have produced water with more than 0.3 mg/L iron are distributed throughout BMU's 3 and 4. 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 NPS contamination significantly contributes to iron concentrations in the project area.

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 EPA primary drinking-water standard for manganese in water supplies because there are no identified, serious health threats posed by it. There is, however, a secondary standard of 0.05 mg/L for manganese based on the fact that higher concentrations may produce objectionable odor, taste, color, corrosion, and staining.

The data repository contained 10,774 manganese measurements ranging from 0.0 to 114 mg/L. In BMU 3, approximately 42 percent (2,074 of 4,964) of the measurements and 42 percent (784 of 1,883) of the sites had manganese concentrations less than 0.05 mg/L. In BMU 4, approximately 42 percent (2,434 of 5,810) of the measurements and 32 percent (771 of 2,414) of the sites had values less than 0.05 mg/ L (Table 17).

Table 17. Summary of manganese measurements (mg/L).

	BMU 3	**BMU 4**
Measurements	4,964	5,810
Sites	1,883	2,414
Maximum	114	98
3rd quartile	0.32	0.40
Median	0.076	0.087
1st quartile	0.011	0.010
Minimum	0.00	0.00
Interquartile range	0.010 to 0.320	0.010 to 0.4000
Sites < 0.05 mg/L	784	771

SMCL = 0.05 mg/L

Cumulative data plots (Figs. 88 and 89) show similar patterns but more measured manganese concentrations greater than 10 mg/L in BMU 4 than in BMU 3.

The Mississippi and Lower Cumberland River watersheds have the lowest range of manganese concentrations (Fig. 90).

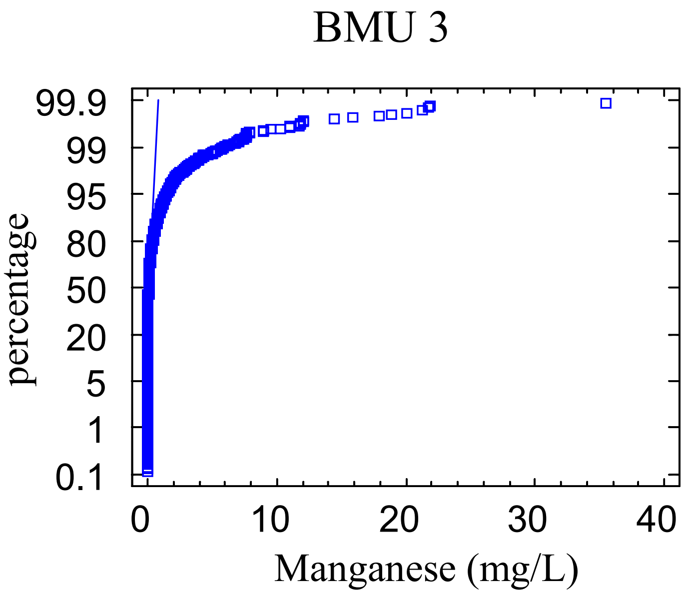


Figure 88. Cumulative plot of manganese values in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. SMCL = 0.05 mg/L.

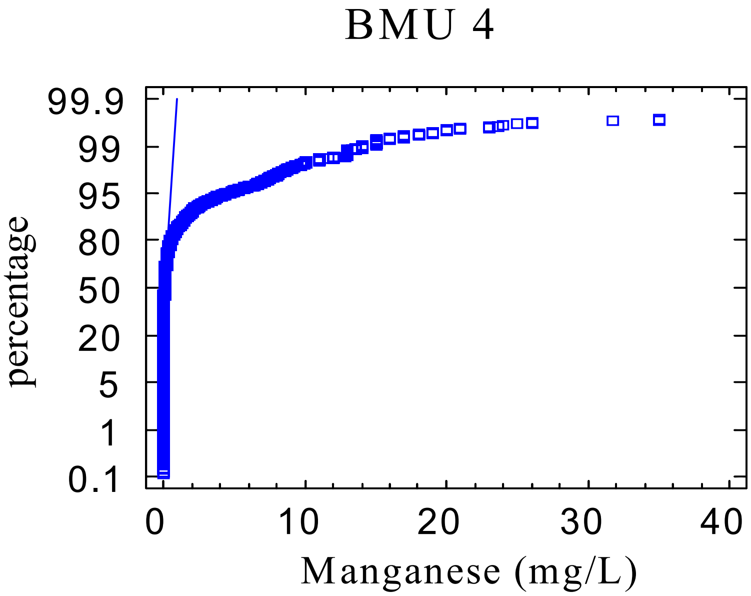


Figure 89. Cumulative plot of manganese values in BMU 4. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly. SMCL = 0.05 mg/L.

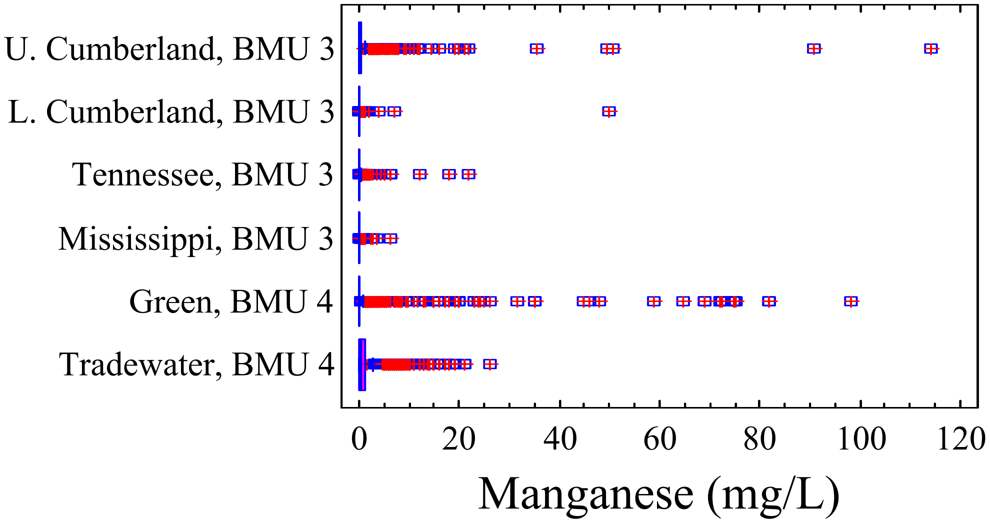


Figure 90. Comparison of manganese values grouped by major watershed. SMCL = 0.05 mg/L.

Figure 91 shows that manganese concentrations above the SMCL occur in both BMU's 3 and 4, in all major watersheds, and in 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. 91) with the map of high iron concentrations (Fig. 83) shows the similar pattern.

Sites in the Eastern and Western Coal Fields have the highest manganese concentrations, whereas sites in the Jackson Purchase and Knobs Regions have the lowest concentrations (Fig. 92).

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. 93), and that high manganese concentrations are less common in groundwater from springs than in well water (Fig. 94). Very high manganese concentrations (> 5 mg/L) are much more common in shallow wells than in groundwater from deeper wells (Fig. 95).

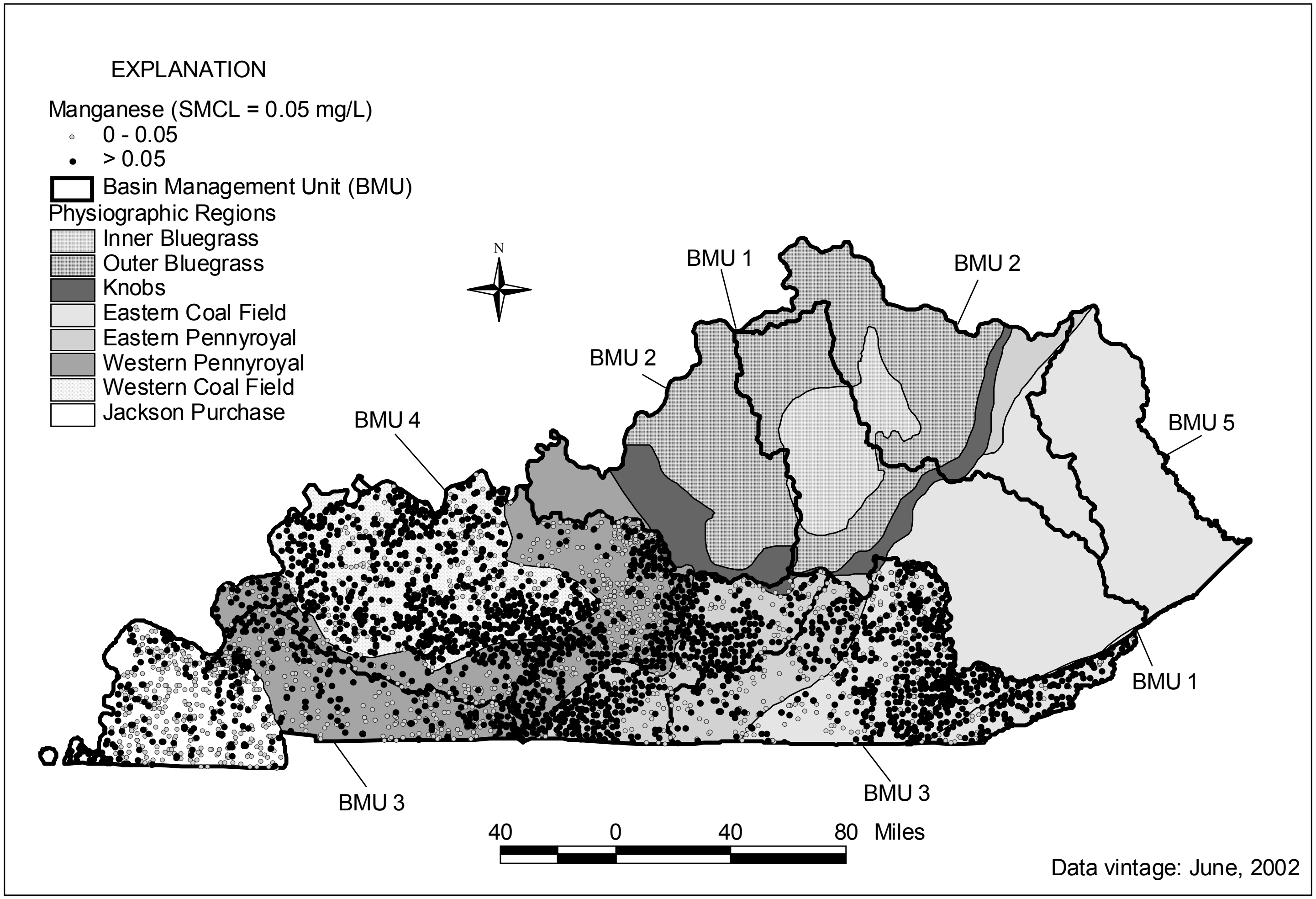


Figure 91. Sample sites and manganese concentrations.

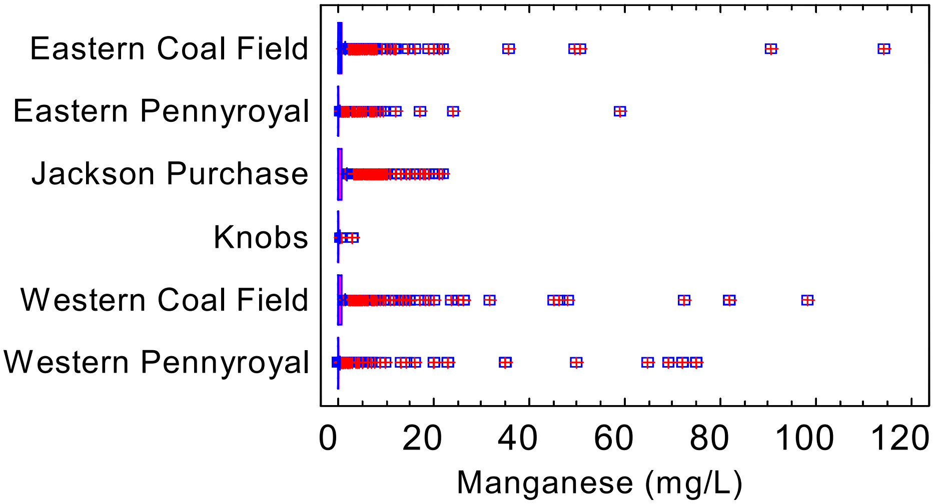


Figure 92. Comparison of manganese values grouped by physiographic region. SMCL = 0.05 mg/L.

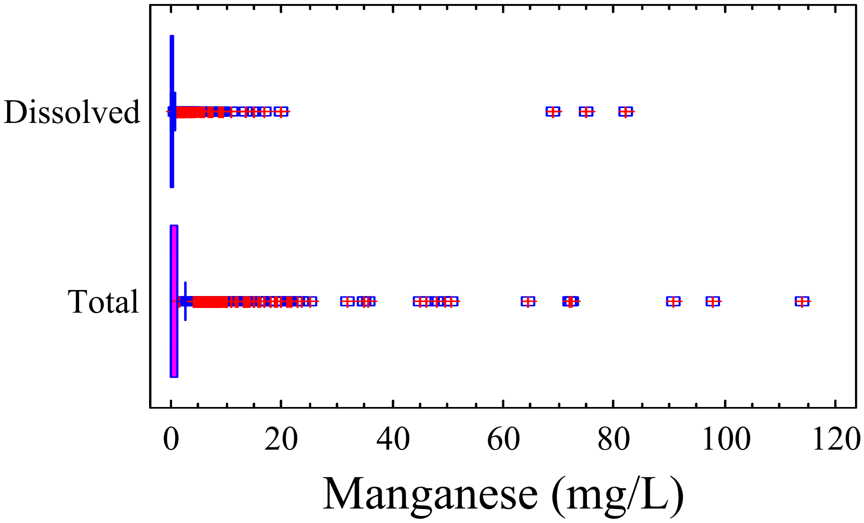


Figure 93. Comparison of total and dissolved manganese values. SMCL = 0.05 mg/L.

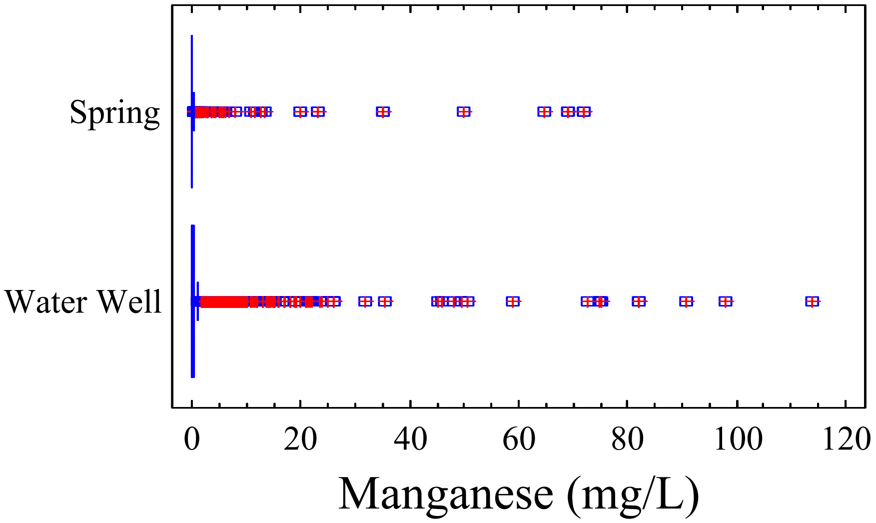


Figure 94. Summary of manganese concentrations grouped by site type. SMCL = 0.05 mg/L.

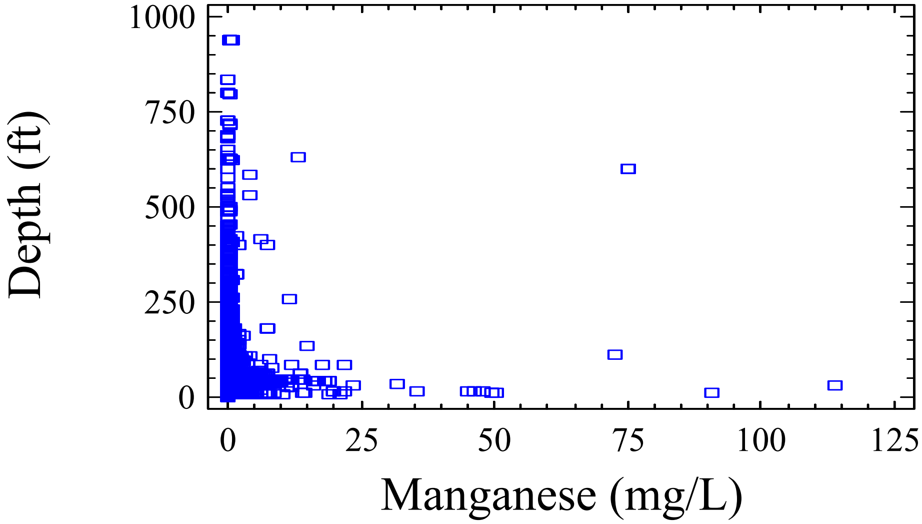


Figure 95. Plot of manganese concentrations versus well depth. SMCL = 0.05 mg/L.

Summary: 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 NPS contamination significantly contributes to manganese concentrations in the project area.

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 exist in a deep, reducing groundwater system.

Runoff from fertilizer use, leachate from septic tanks, and sewage are common sources of nitrogen species. Nitrate is commonly used as fertilizer; high nitrate concentrations generally indicate contamination by fertilizer or by either human or animal organic waste. Caves in karst terrane that are home to large bat colonies may accumulate large amounts of guano that contributes 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^+). However, analyses for environmental purposes generally report the concentrations as equivalent amounts of nitrogen (nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, or ammonium-nitrogen). Consequently, reported 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) because higher concentrations can lead to methemoglobinemia (blue baby syndrome) in infants, where 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. However, ammonia concentrations of 1 to 10 mg/L can be toxic to aquatic life.

Nitrate-Nitrogen

The data repository contained 10,317 nitrate-nitrogen measurements at 2,469 sites (Table 18). The maximum values in both regions far exceed the MCL of 10 mg/L. However, the third-quartile and median values are below the MCL in both regions. The median nitrate-nitrogen value in BMU 3 is significantly greater than the median value in BMU 4, and the interquartile range of values is greater in BMU 3 than in BMU 4. About 6 percent (90 of 1,399) of the sites in BMU 3 and 8 percent (89 of 1,070) of the sites in BMU 4 yielded water with nitrate-nitrogen greater than 10 mg/L. BMU 3 has more sites where nitrate-nitrogen approaches the MCL: about 79 percent of the sites in BMU 3 (1,111 of 1,399), and 21 percent (222 of 1,070) of the sites in BMU 4 yielded water with nitrate-nitrogen greater than 5 mg/L (Table 18).

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

	BMU 3	**BMU 4**
Measurements	6,911	3,406
Sites	1,399	1,070
Maximum	449	110.7
3rd quartile	5.31	1.40
Median	4.38	0.63
1st quartile	1.11	0.20
Minimum	0.00	0.00
Interquartile range	1.11 to 6.31	0.20 to 1.40
Sites > 10.0	90	89
Sites > 5.0	1,111	222

MCL = 10 mg/L as N

The data distribution for measurements from BMU 3 suggests the presence of two different populations of values, whereas the distribution of data from BMU 4 has a more typical shape (Figs. 96–97). This probably reflects the diverse physiographic regions and resulting land uses (mining, forestry, and agriculture) in BMU 3, whereas the major land use in BMU 4 is predominantly agricultural.

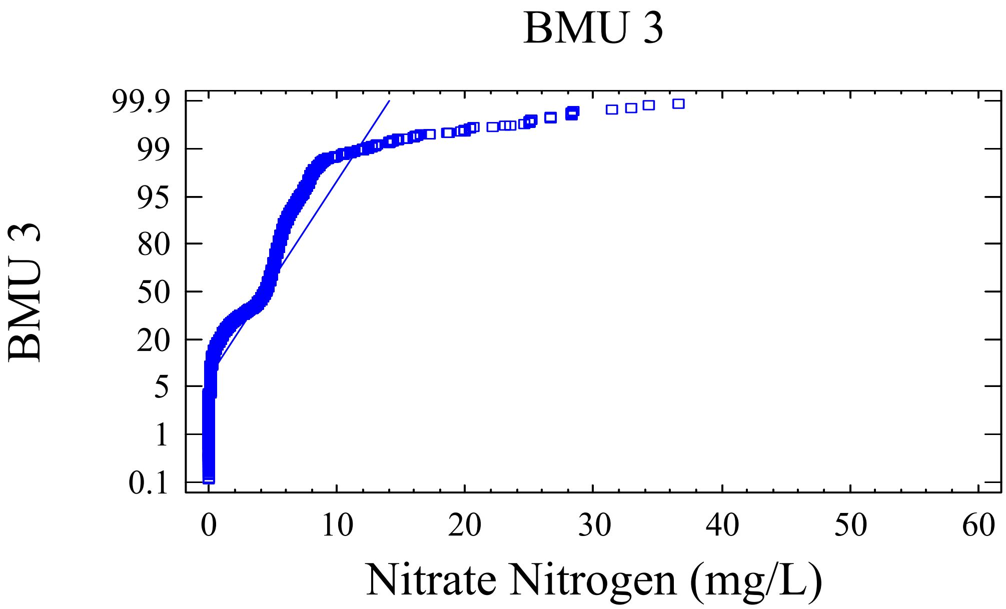


Figure 96. Cumulative plot of nitrate-nitrogen concentrations from BMU 3. Values greater than 60 mg/L have been omitted to show detail in the lower concentration ranges. MCL = 10 mg/L as N.

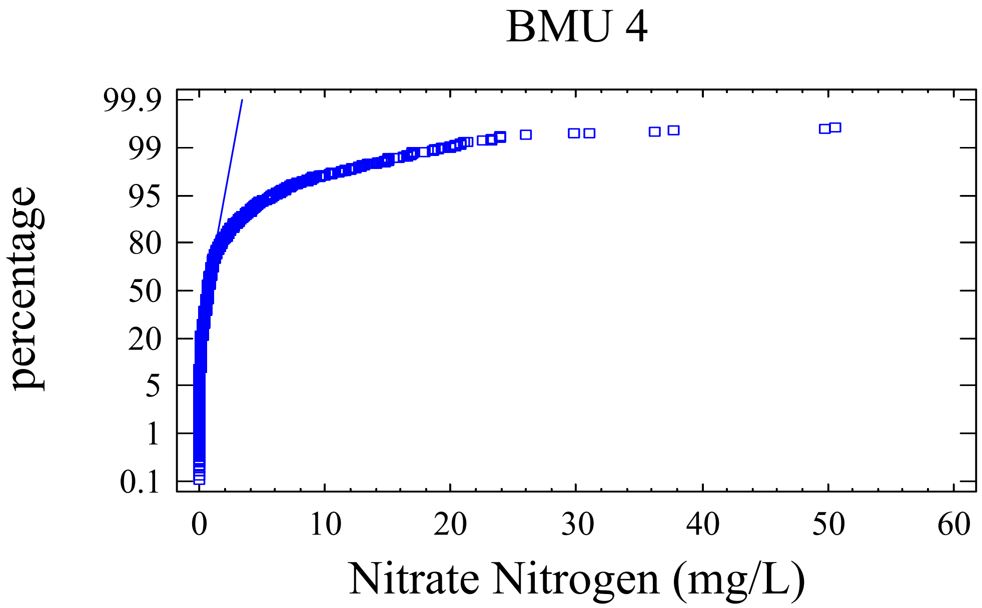


Figure 97. Cumulative plot of nitrate-nitrogen concentrations from BMU 4. Values greater than 60 mg/L have been omitted to show detail in the lower concentration ranges. MCL = 10 mg/L as N.

Grouping nitrate concentrations by major watershed (Fig. 98), mapping sites, and concentration ranges (Fig. 99), and grouping the results by physiographic region (Fig. 100) shows that concentrations exceeding the MCL occur in all watersheds and regions. All major watersheds contain sites where nitrate concentrations exceed the MCL, and the interquartile ranges are similar. However, the median nitrate concentration is significantly higher in the Lower Cumberland watershed and Western Pennyroyal Region of BMU 3 than elsewhere (Figs. 98 and 100). The Jackson Purchase Region is much more heavily sampled than other parts of the project area; sample sites in the Eastern and Western Coal Fields are relatively sparse (Fig. 99).

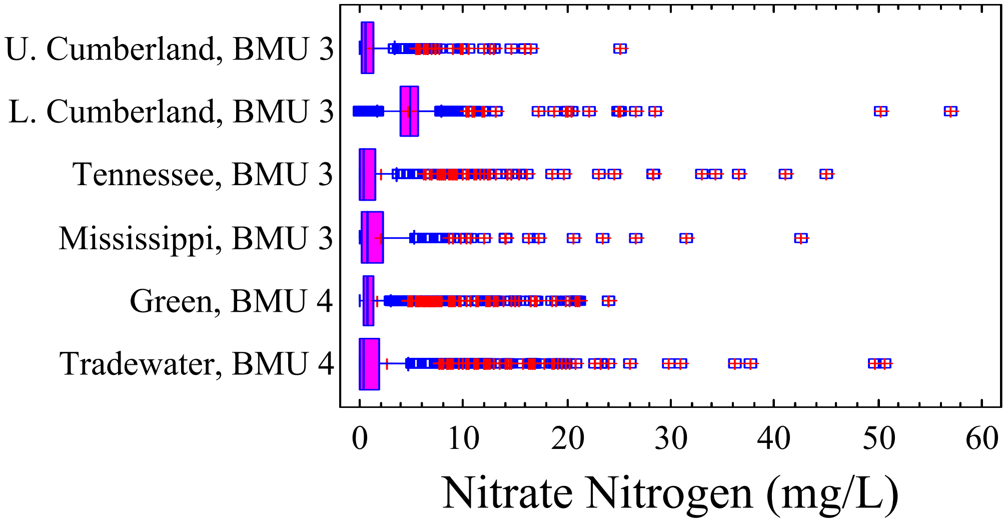


Figure 98. Summary of nitrate measurements grouped by major watershed. Values greater than 60 mg/L were omitted to show detail in the lower concentration ranges. MCL = 10 mg/L as N.

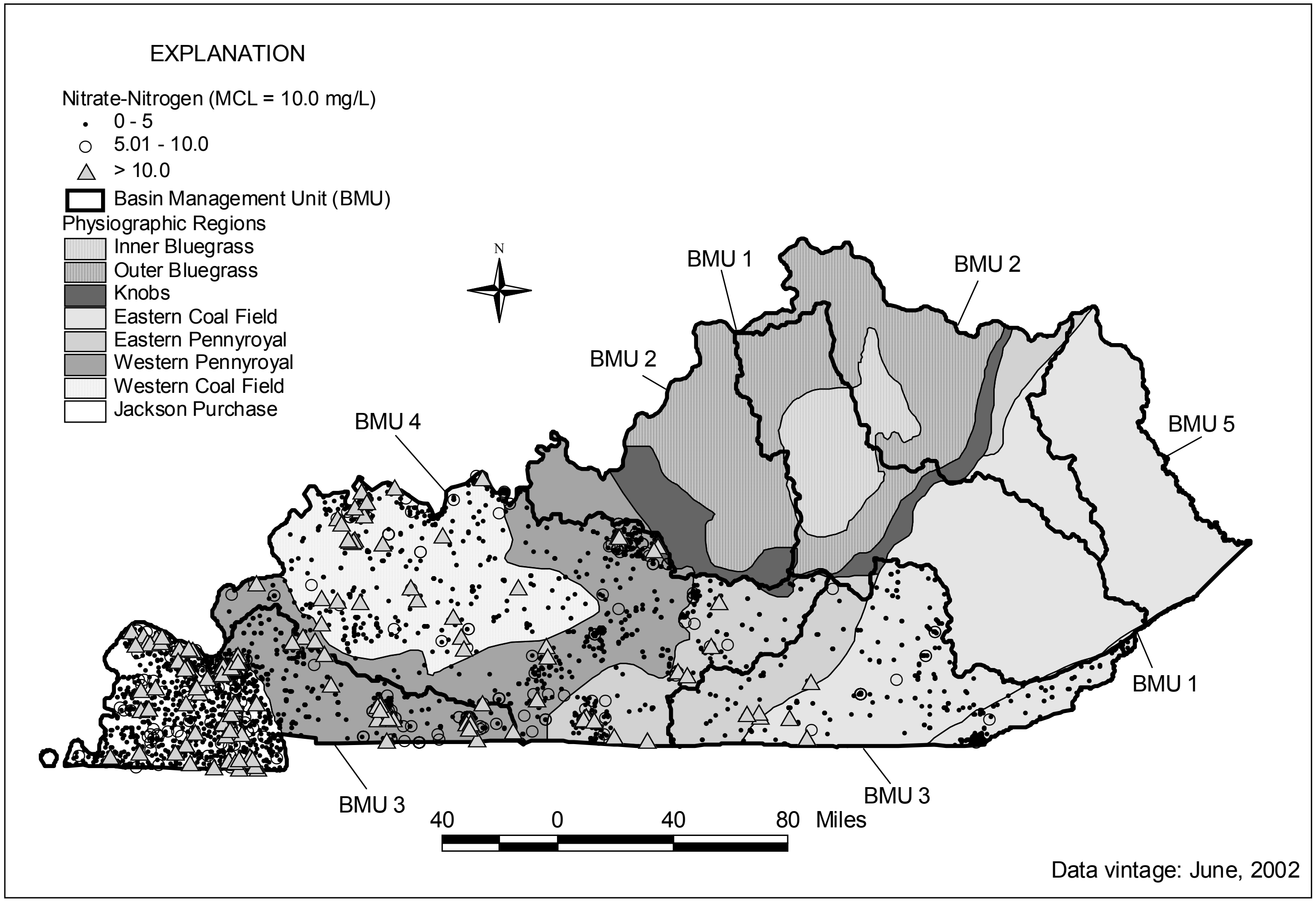


Figure 99. Map showing sample sites and nitrate-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

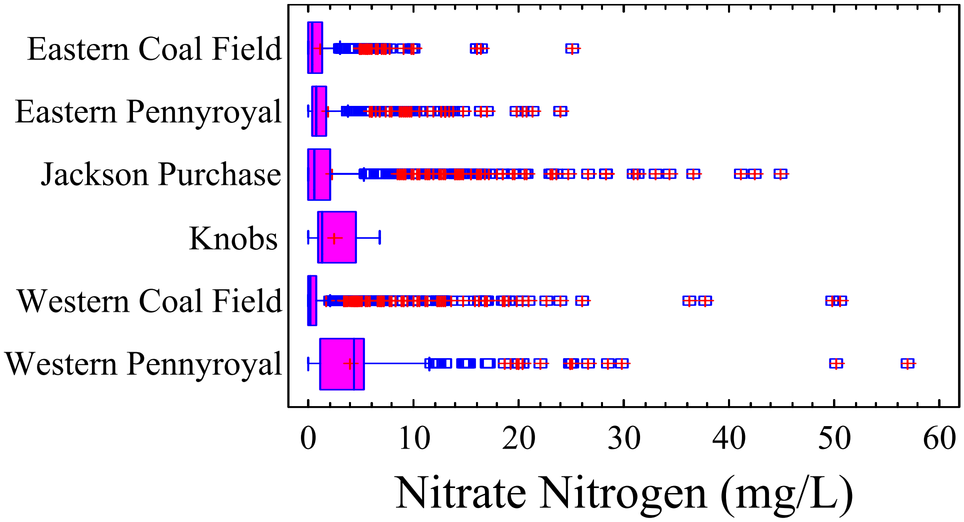


Figure 100. Summary of nitrate-nitrogen data grouped by physiographic region. Values greater than 60 mg/L were omitted to show detail in the lower concentration ranges. MCL = 10 mg/L as N.

Water wells yielded the highest nitrate concentrations (Fig. 101), and shallow wells are more likely to produce groundwater with high nitrate concentrations than are deeper wells (Fig. 102).

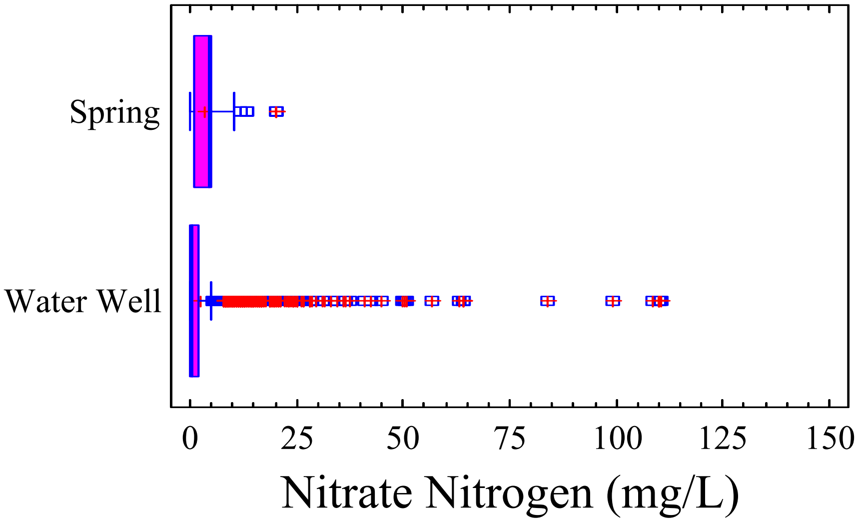


Figure 101. Summary of nitrate concentrations grouped by site type. MCL = 10 mg/L as N.

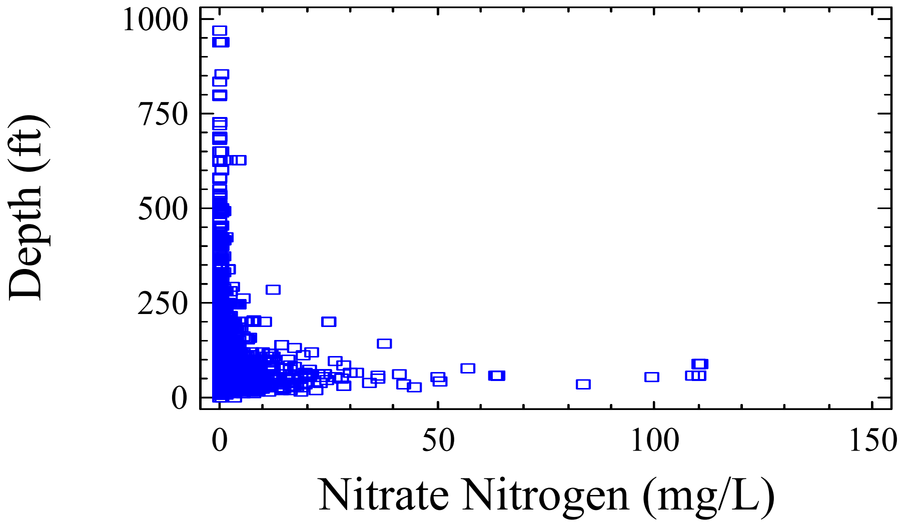


Figure 102. Plot of nitrate concentrations versus well depth. MCL = 10 mg/L as N.

Summary: In the project area, approximately 7 percent of all sites produced groundwater with nitrate-nitrogen concentrations that exceed the EPA health-based standard. Land use around each site would have to be examined to assign a nitrate source with certainty. However, it is highly probable that all these sites are areas where agricultural chemicals are used, animal holding facilities exist, or sewage is disposed. 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 NPS 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 is available (Conrad and others, 1999a) and can be viewed on the KGS Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

Nitrite-Nitrogen

The data repository contained 1,598 measurements of nitrite-nitrogen from 226 sites (Table 19). No reported concentrations exceeded the EPA health-based MCL of 1.0 mg/L. With the exception of the maximum values, nitrite-nitrogen measurements are similar in BMU 3 and BMU 4 (Table 19 and Fig. 103).

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

	BMU 3	**BMU 4**
Measurements	703	895
Sites	112	114
Maximum	0.274	0.753
3rd quartile	0.009	0.010
Median	0.005	0.005
1st quartile	0.002	0.002
Minimum	0.000	0.000
Interquartile range	0.002 to 0.009	0.002 to 0.010

MCL = 1.0 mg/L as N

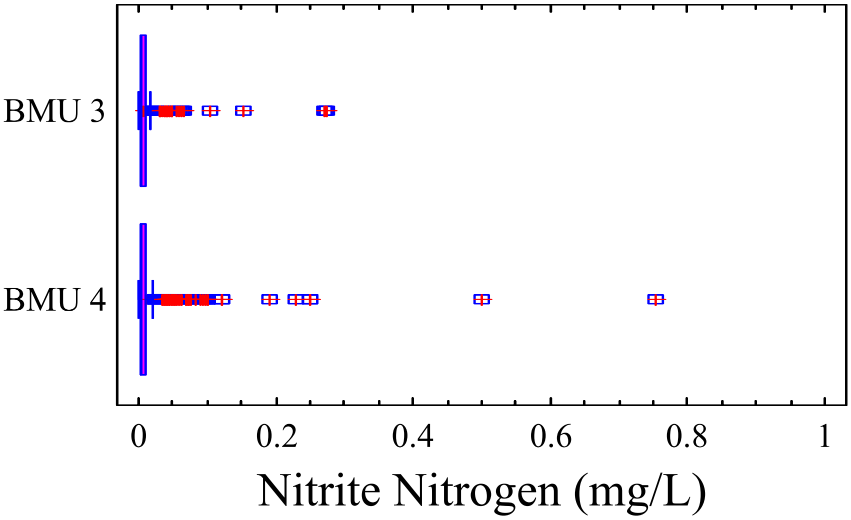


Figure 103. Summary of nitrite measurements grouped by BMU. MCL = 1.0 mg/L as N.

The map (Fig. 104) shows that relatively few sites have been sampled for nitrite-nitrogen. Because of the sparse data and the absence of any reported concentration that exceeded the MCL, no further analyses were performed.

Summary: No sites in the project area produced groundwater with nitrite-nitrogen concentrations over the EPA 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.

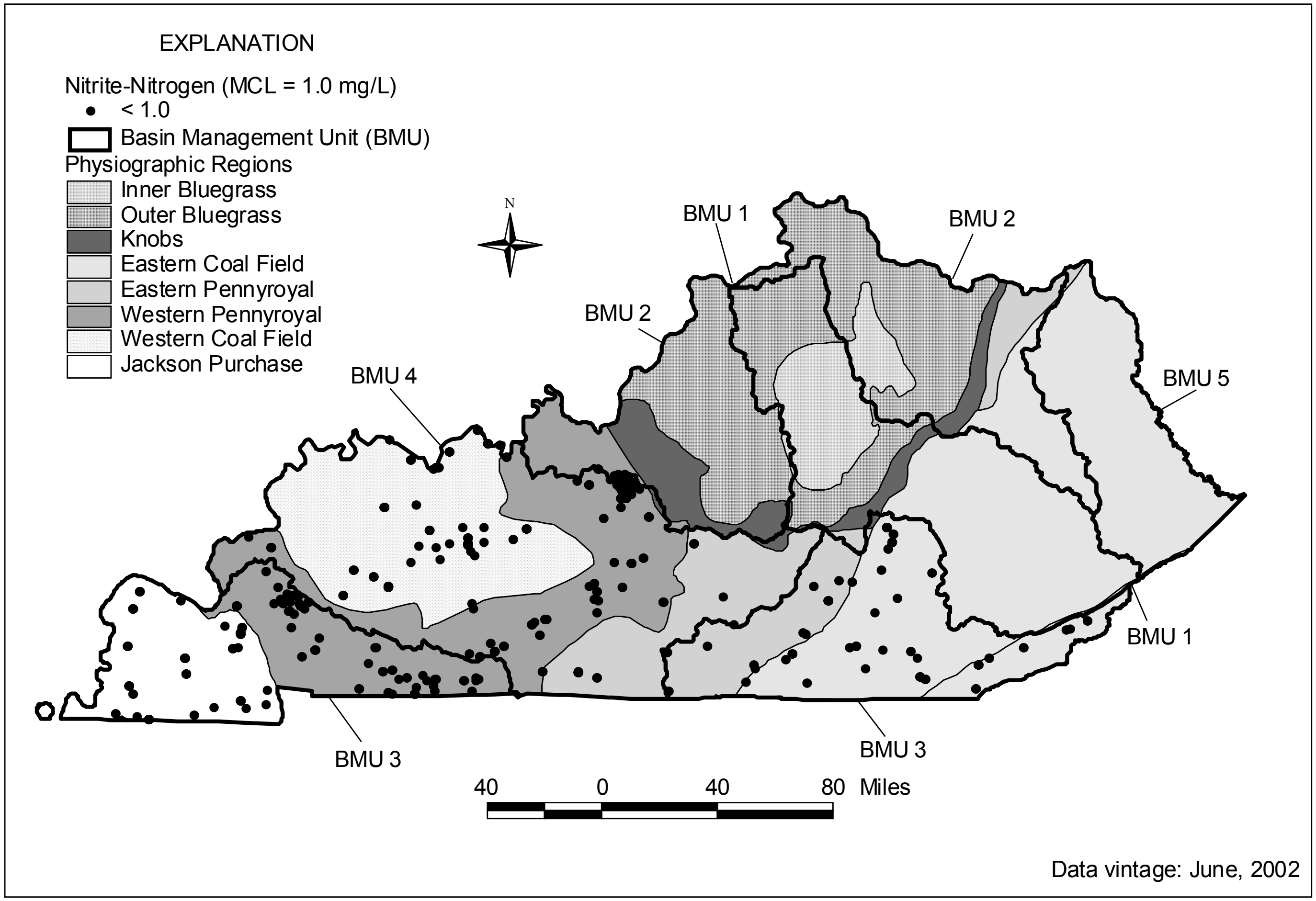


Figure 104. Map showing sites where nitrite-nitrogen has been measured.

Ammonia-Nitrogen

The data repository contained 1,944 ammonia-nitrogen measurements from 271 sites in the project area (Table 20). Although there are no EPA health-based standards for ammonia-nitrogen, the Kentucky Department for Environmental Protection (DEP) has recommended a risk-based upper limit of 0.110 mg/L. Values exceeding 0.110 mg/L were observed at 36 sites in BMU 3 and 190 sites in BMU 4.

Table 20. Summary of ammonia-nitrogen measurements (mg/L of N).

	BMU 3	**BMU 4**
Measurements	811	1,133
Sites	113	158
Maximum	14.7	7.02
3rd quartile	< 0.050	< 0.050
Median	< 0.020	< 0.050
1st quartile	< 0.020	< 0.002
Minimum	0.000	0.000
% sites > 0.110	15	26

DEP = 0.110 mg/L as N

Cumulative probability plots (Figs. 105–106) show a greater number of high ammonia-nitrogen measurements in BMU 4 compared to BMU 3. Ammonia-nitrogen measurements that exceed 0.110 mg/L are found in both BMU's 3 and 4, in all physiographic regions, and in all major watersheds. Sites where these values are observed are clustered in the Eastern Coal Field of the Upper Cumberland River Basin and near the eastern corner of the Lower Cumberland River Basin in the Western Pennyroyal, and are distributed throughout the Western Coal Field (Green and Tradewater watersheds) and the Jackson Purchase (Tennessee and Mississippi watersheds) (Figs. 107–109).

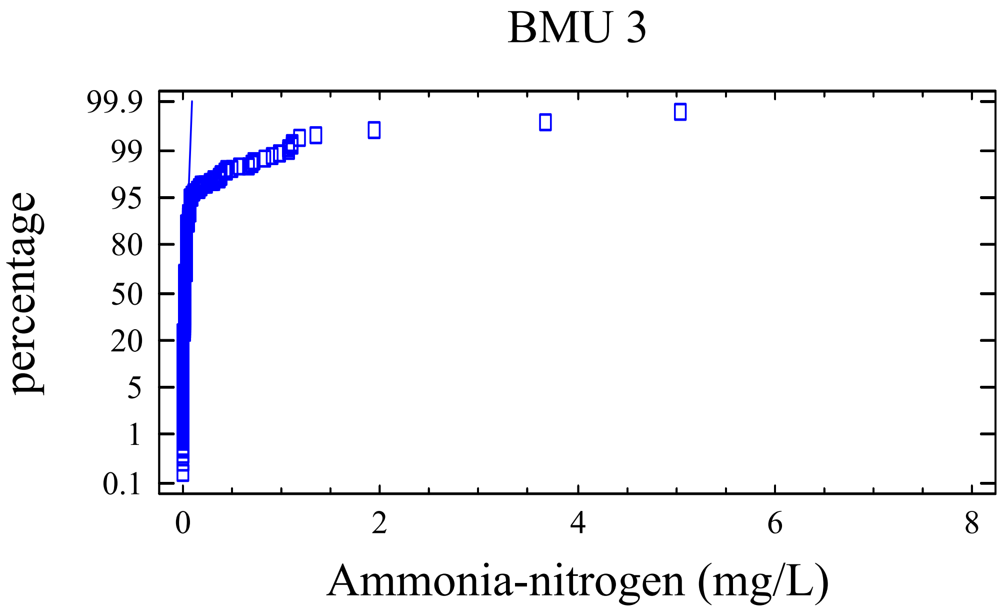


Figure 105. Cumulative plot of ammonia-nitrogen measurements from BMU 3. DEP = 0.110 mg/L as N.

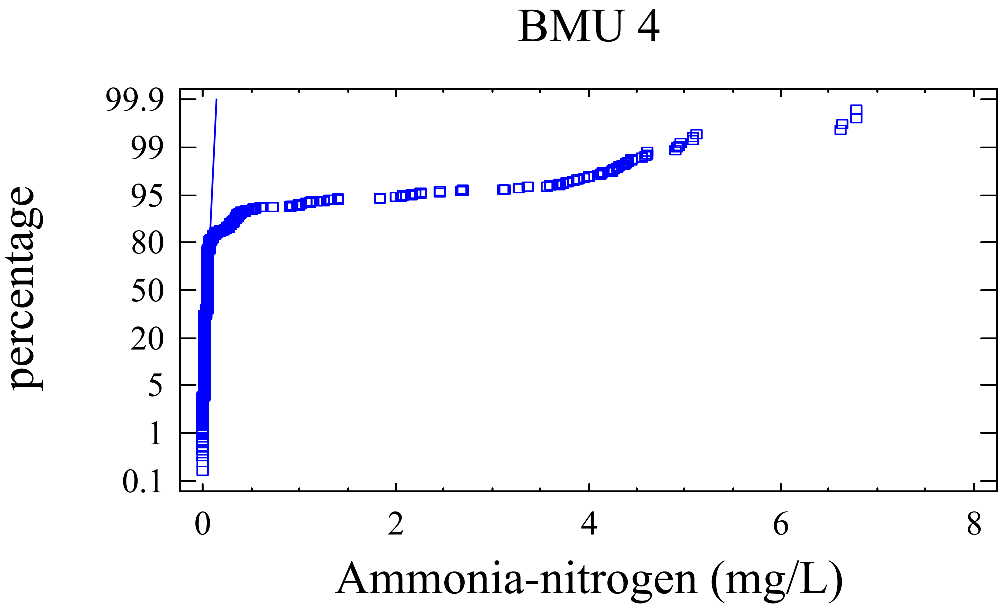


Figure 106. Cumulative plot of ammonia-nitrogen measurements from BMU 4. DEP = 0.110 mg/L as N.

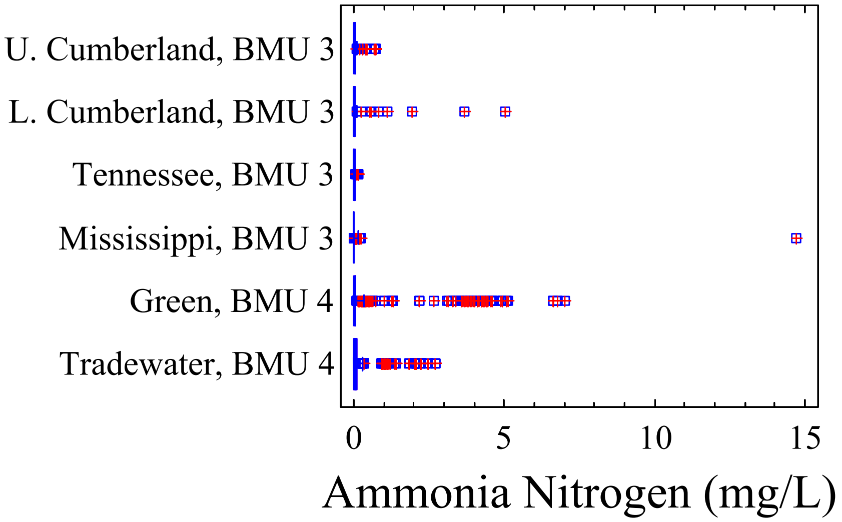


Figure 107. Ammonia-nitrogen data grouped by major watershed. DEP = 0.110 mg/L as N.

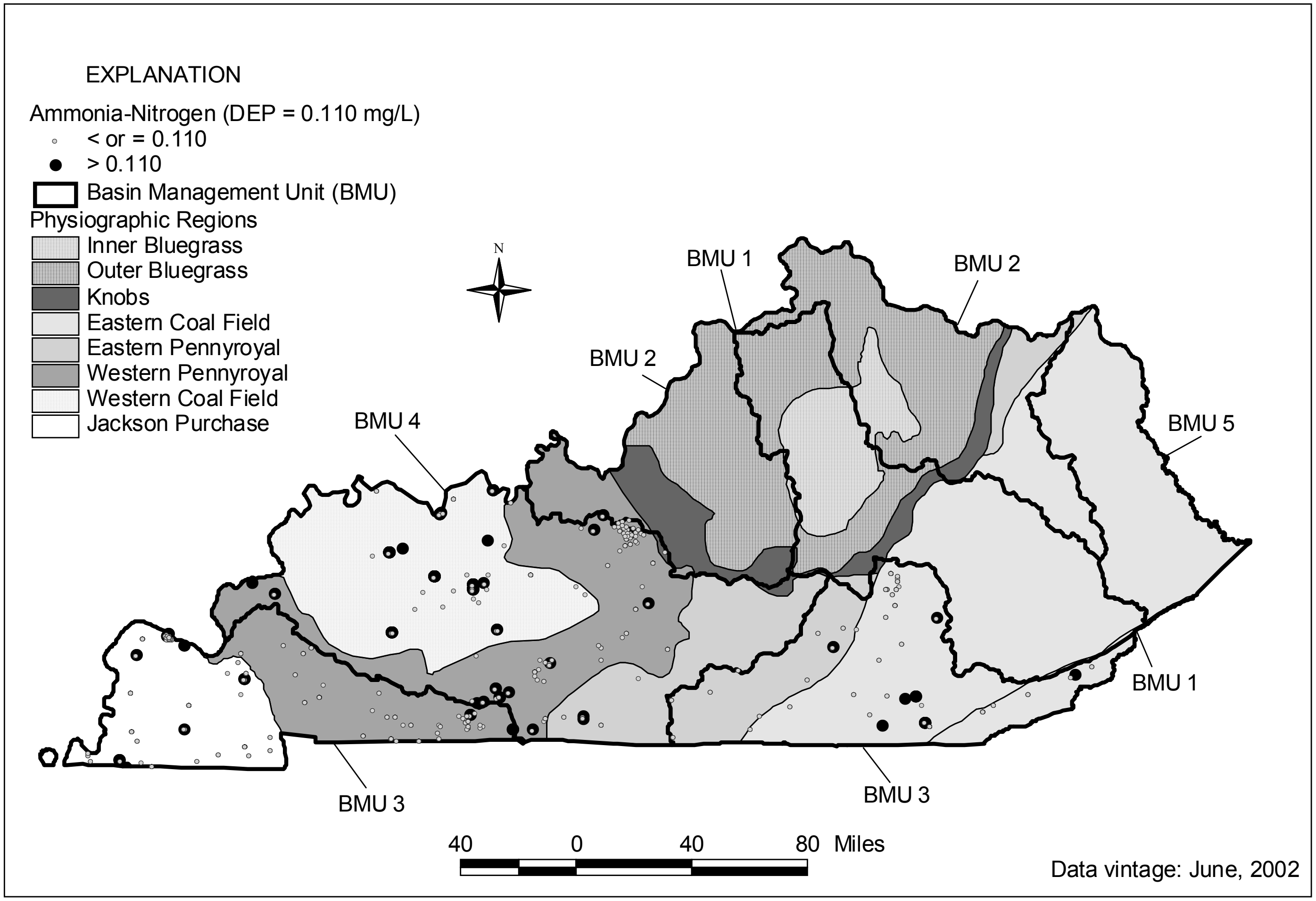


Figure 108. Map showing sample sites and ammonia-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

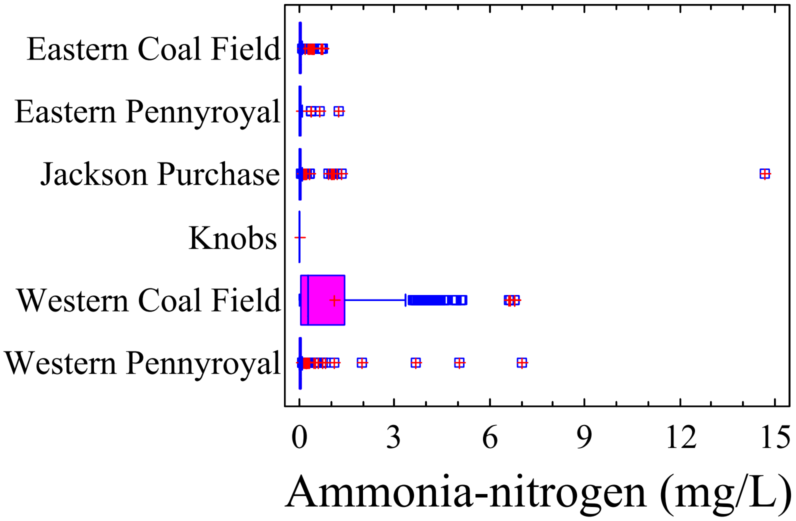


Figure 109. Ammonia-nitrogen data grouped by physiographic region. DEP = 0.110 mg/L as N.

High ammonia-nitrogen values are more commonly found in wells rather than in springs (Fig. 110) and are more common in shallow wells than in intermediate or deep wells (Fig. 111).

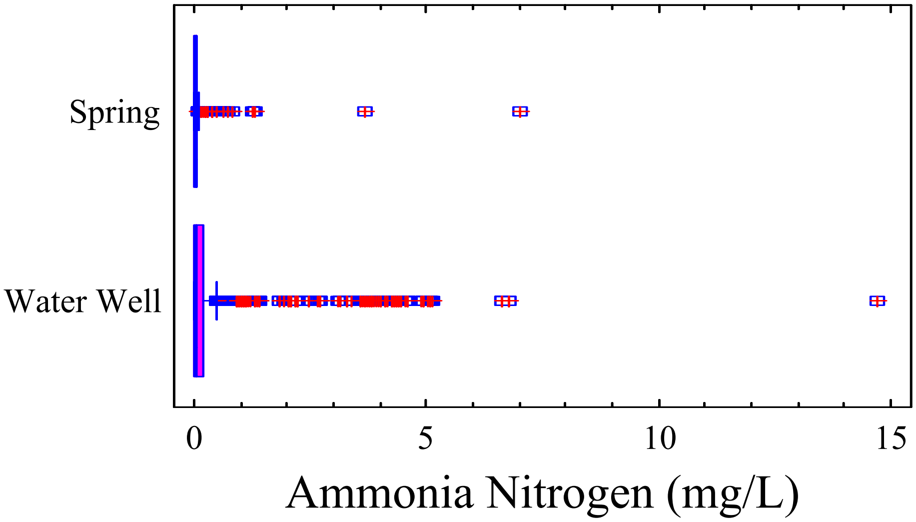


Figure 110. Summary of ammonia-nitrogen data grouped by site type. DEP = 0.110 mg/L as N.

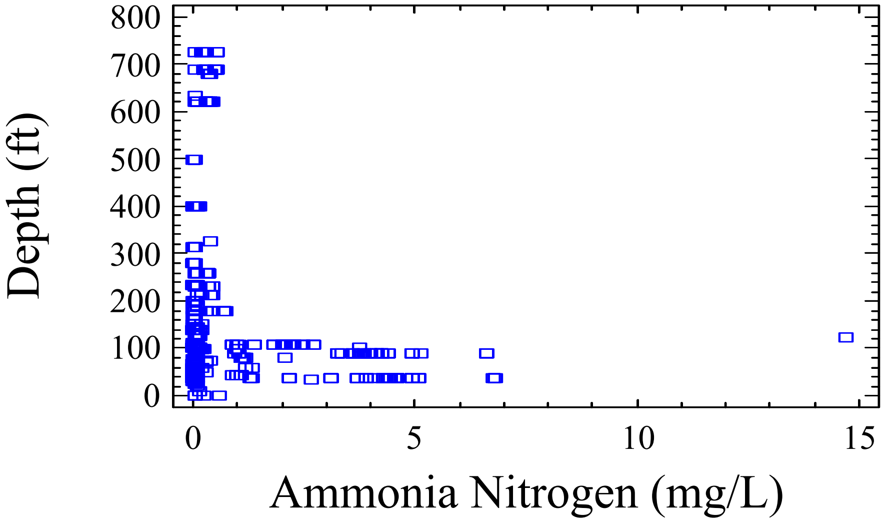


Figure 111. Plot of ammonia-nitrogen concentrations versus well depth. DEP = 0.110 mg/L as N.

Summary: Approximately 21 percent of the sampled wells and springs produced groundwater with more than 0.110 mg/L ammonia-nitrogen. Such high ammonia-nitrogen concentrations were most common in watersheds of the Tradewater and Green Rivers in the Western Coal Field. The source of ammonia-nitrogen in these groundwaters cannot be established definitely without additional information. However, NPS contributions from agriculture, confined animal feeding operations, or septic systems are certainly possible.

Phosphorus Species

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

Phosphorus is an important nutrient and commonly is the limiting nutrient in aquatic ecosystems. The most important anthropogenic 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) as $H_2PO_4^-$ or HPO_4^{-2} is the most common form of phosphorus in most natural waters (Hem, 1985). The specific form of orthophosphate is pHdependent, but normal sample collection and analysis procedures report all phosphate determined on a filtered sample as total orthophosphate. Phosphorus may 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 due to organic particulate phosphorus.

There are no health-based water-quality standards for phosphorus species in water. 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, and that total phosphorus be less than 0.1 mg/L, based on results from the U.S. Geological Survey National Water-Quality Assessment Program.

Orthophosphate Phosphorus

The data repository contained 909 orthophosphate measurements in BMU's 3 and 4 (Table 21). Of the 170 measurements from BMU 3, 123 were reported as "less than 0.059 mg/L." Whether these samples exceeded the recommended water-quality standard of 0.04 mg/L cannot be determined, because the analytical detection limit was higher than the water-quality standard. Only 11 measurements at seven sites are known to exceed the water-quality standard in BMU 3. This uncertainty does not apply to samples from BMU 4, because the analytical detection limit for those analyses was 0.003 mg/L.

Table 21. Orthophosphate-P measurements (mg/L of P).

	BMU 3	**BMU 4**
Measurements	170	739
Sites	67	53
Maximum	0.495	3.949
3rd quartile	< 0.059	0.103
Median	< 0.059	0.046
1st quartile	< 0.059	0.022
Minimum	< 0.019	< 0.003
Sites with values greater than 0.04	7*	46

<: analytical result reported as "less than" the stated value.
*: see discussion in text

Cumulative data plots (Figs. 112–113) show that few values greater than 0.2 mg/L have been reported from BMU 3, whereas such values are common in BMU 4.

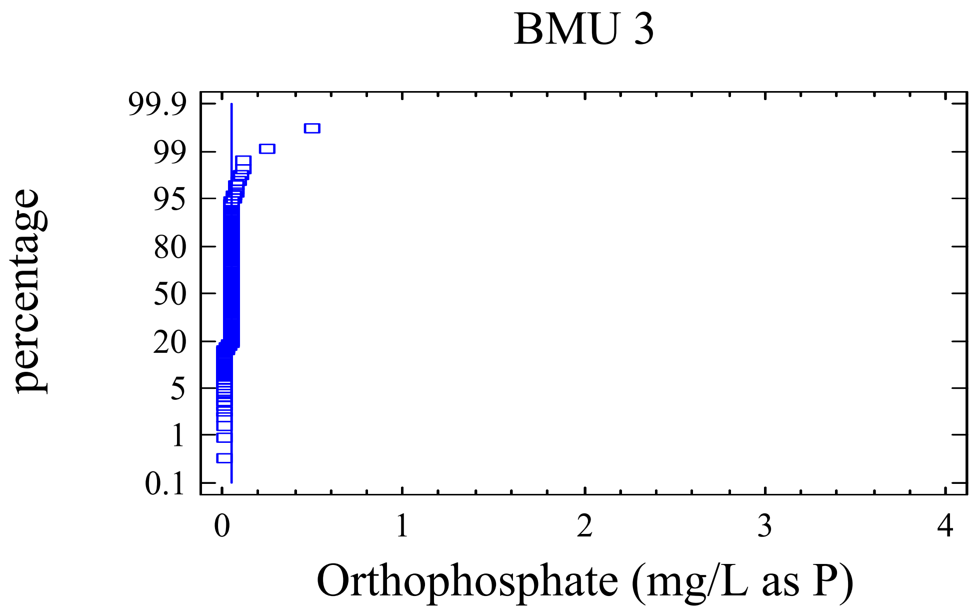


Figure 112. Cumulative plot of orthophosphate values in BMU 3.

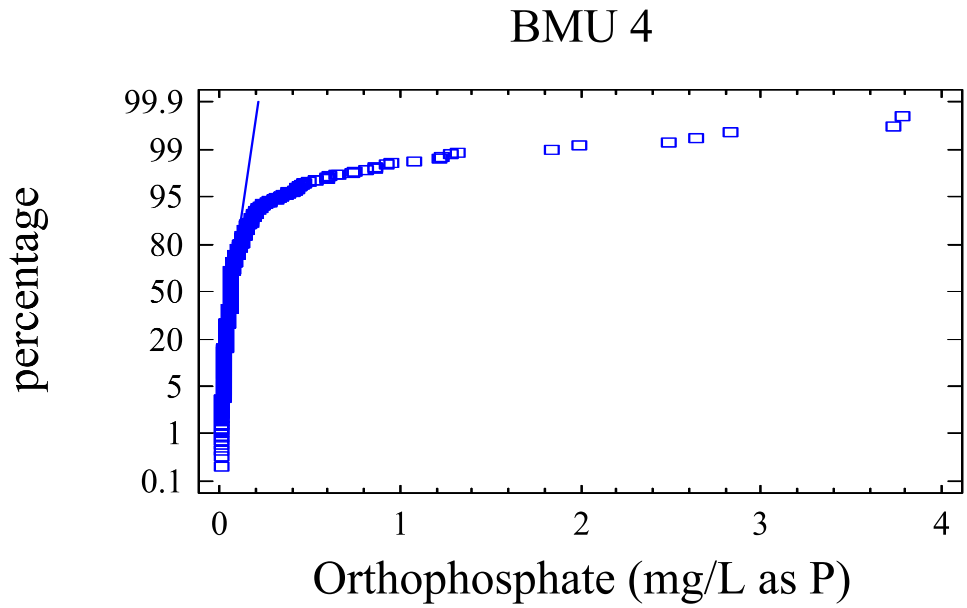


Figure 113. Cumulative plot of orthophosphate values in BMU 3.

The map (Fig. 114) shows sampled sites and locations where measured orthophosphate-P concentrations exceeded 0.04 mg/L. Values greater than 0.04 mg/L as P are common in the Western Pennyroyal, which includes parts of the watersheds of the Lower Cumberland, Tradewater, and Green Rivers, and in the Western Coal Field, which includes the watersheds of the Green and Tradewater Rivers. Wells and springs in the Jackson Purchase, Eastern Coal

Field, and Eastern Pennyroyal had relatively few orthophosphate concentrations that exceeded the recommended concentration of 0.04 mg/L.

As was the case for other nutrients, high orthophosphate concentrations are more likely to be reported from wells than from springs (Fig. 115), and are more likely to be reported from shallow groundwater systems than from deeper flow regimes (Fig. 116).

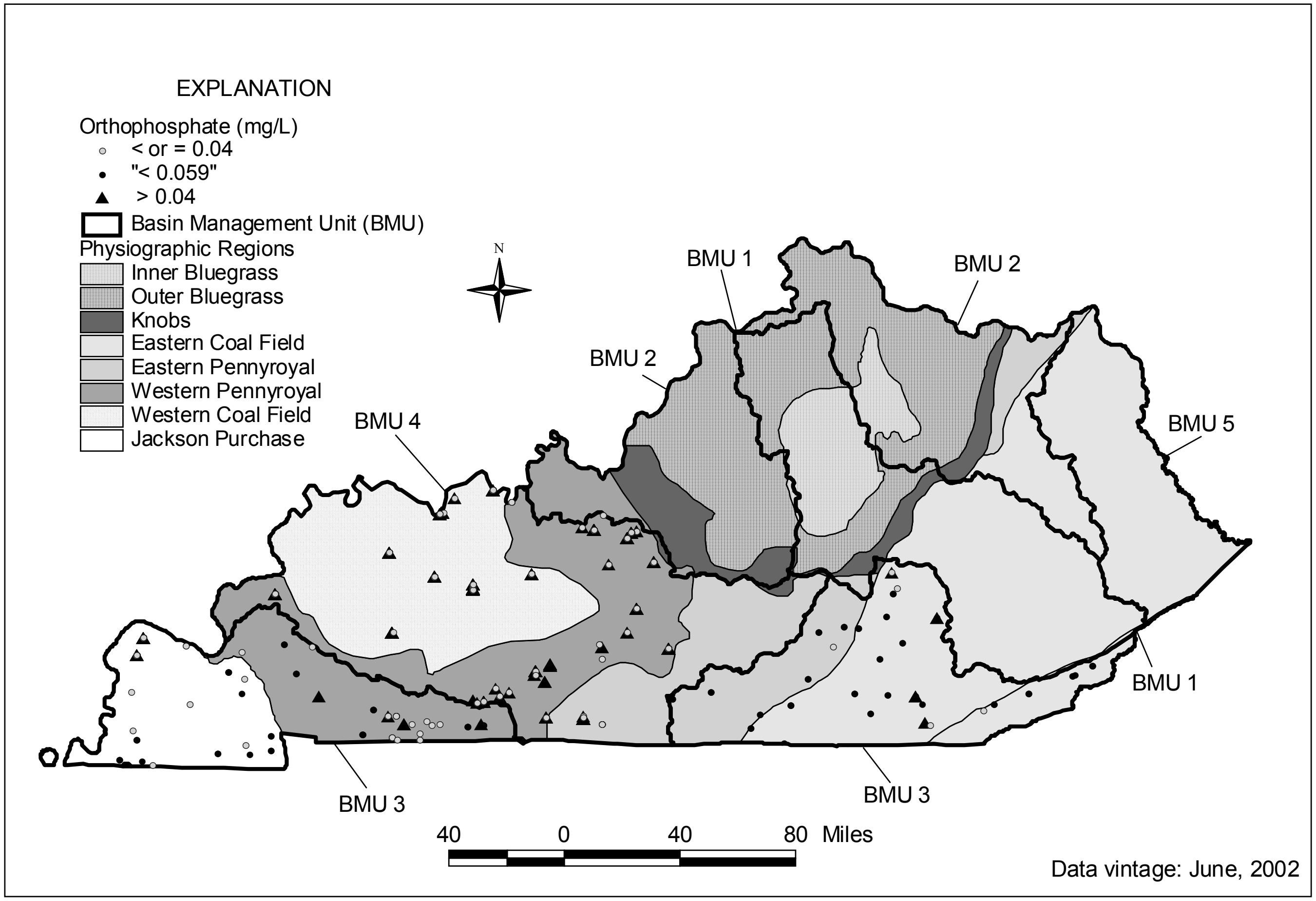


Figure 114. Map showing sample sites and orthophosphate-P values. Superimposed symbols indicate that values recorded at different collection times fell into different ranges.

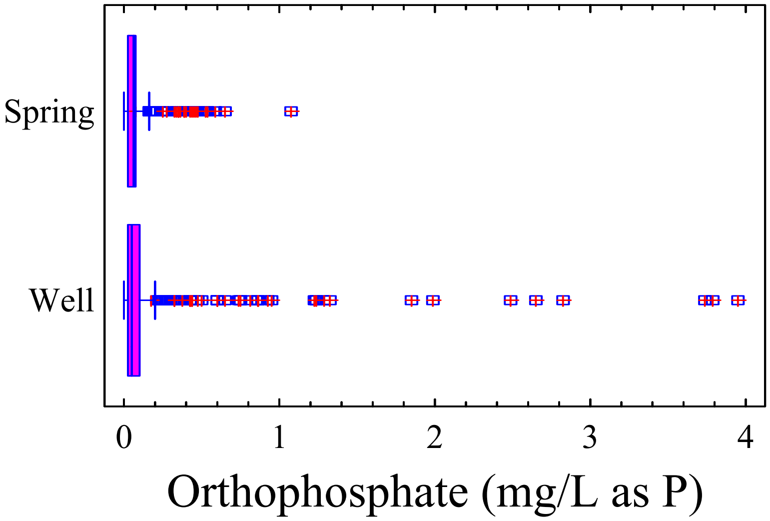


Figure 115. Plot of orthophosphate values grouped by site type.

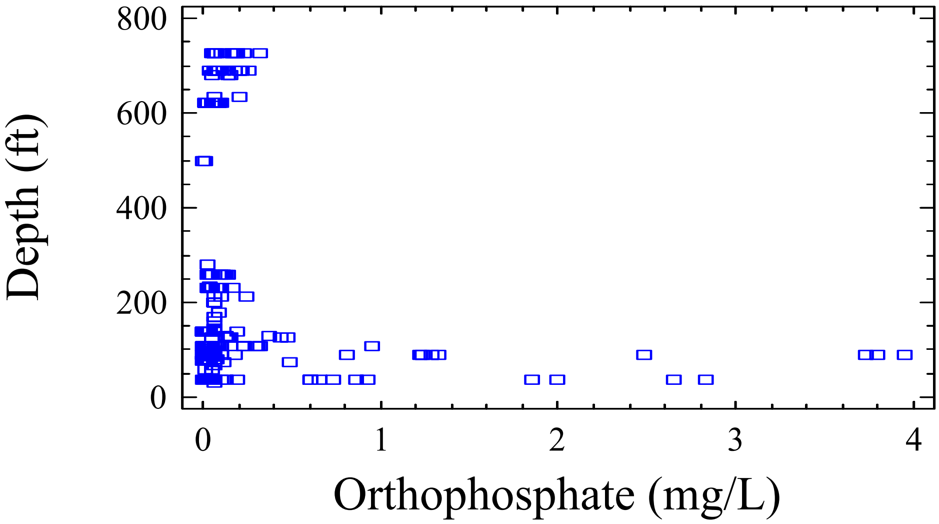


Figure 116. Plot of orthophosphate values versus well depth.

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 seven sites yielded groundwater with measured orthophosphate-phosphorus concentrations that exceeded the water-quality standard. In contrast, nearly 85 percent of the sampled wells and springs in BMU 4 yielded groundwater that had more than 0.04 mg/L orthophosphate-phosphorus. Most of these sites were in the Western Coal Field and the Ohio River alluvium adjacent to the coal field. Nonpoint-source contributions of orthophosphate nutrients to groundwater is probably minor in BMU 3, but likely in agricultural regions of the limestone Pennyroyal regions and the Western Coal Field.

Total Phosphorus

The database contained 1,402 reports of total phosphorus at 189 sites (Table 22). Nearly three-quarters of the sampled sites were in BMU 4. The maximum total phosphorus measurement was an order of magnitude greater in BMU 3 than in BMU 4 (93.9 vs. 9.1 mg/L as P). This may be a reporting error, but there is no way it can be determined from records in the data repository. The second highest value in BMU 3 was only 3.9 mg/L. Other quartile values were similar in BMU 3 and BMU 4. DOW has proposed a value of 0.1 mg/L as P as the groundwater-quality standard, based on information from the U.S. Geological Survey National Water-Quality Assessment Program.

Three sites in BMU 3 had 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 concern (0.1 mg/L). One of these sites had also yielded 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. It is likely that the actual total phosphorus concentrations at these sites were less than the recommended value of 0.1 mg/L, but this cannot be determined with certainty.

Table 22. Summary of total phosphorus measurements (mg/L of P).

	BMU 3	**BMU 4**
Measurements	443	959
Sites	48	141
Maximum	93.92	9.131
3rd quartile	< 0.08	0.047
Median	0.024	0.020
1st quartile	0.008	0.010
Minimum	0.005	0.000
Sites with values > 0.10	22	30

DOW = 0.1 mg/L as P

Cumulative data plots (Figs. 117–118) show a similar distribution of reported values in BMU 3 and BMU 4.

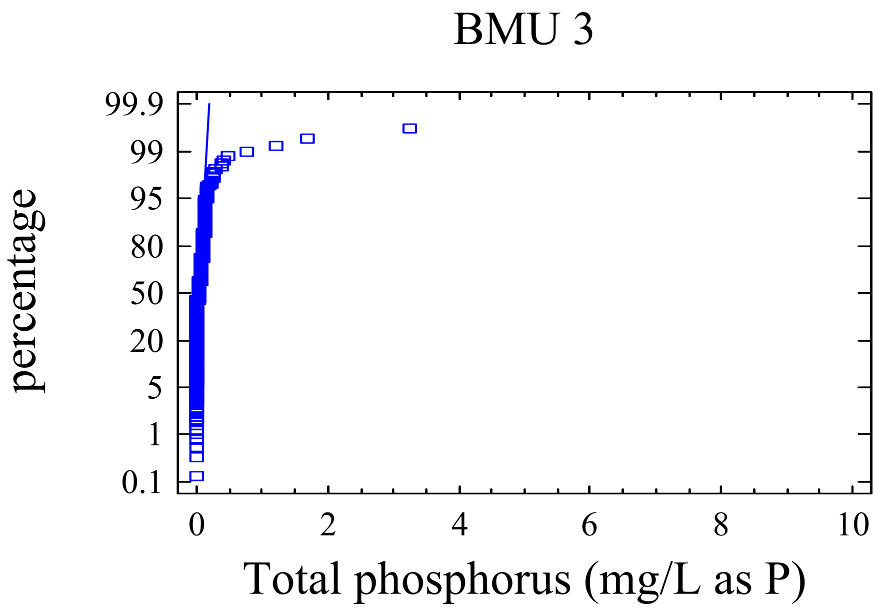


Figure 117. Cumulative plot of total phosphorus measurements from BMU 3. The extreme value of 93.9 mg/L has been excluded to better show the majority of the results. DOW = 0.1 mg/L.

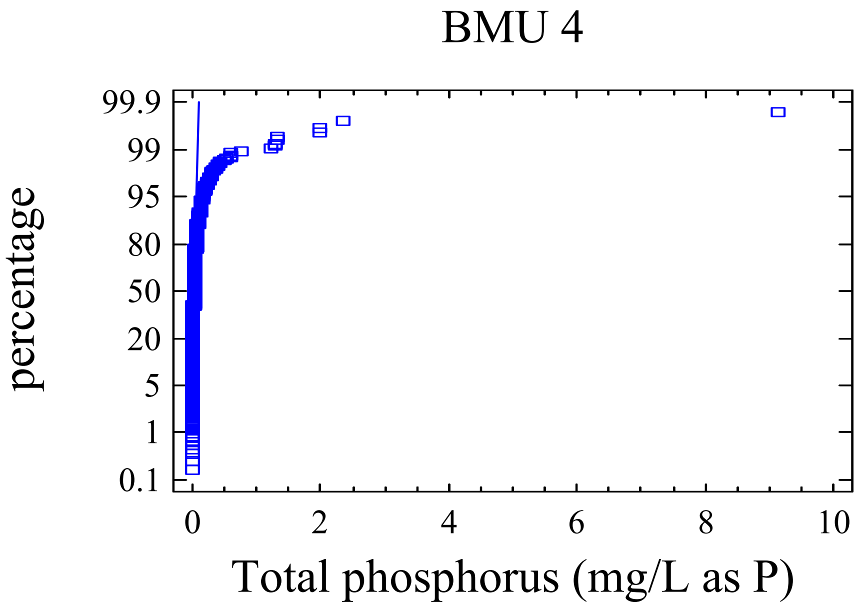


Figure 118. Cumulative plot of total phosphorus measurements from BMU 4. DOW = 0.1 mg/L.

Grouping the results by major watershed (Fig. 119), mapping sample sites and concentration ranges (Fig. 120), and grouping the results by physiographic region (Fig. 121) shows that values exceeding 0.1 mg/L were reported from sites throughout the project area. Such sites are clustered in the northeastern (Green River Basin) and south-central (Green and Lower Cumberland River Basins) portions of the Western Pennyroyal, and randomly distributed through the rest of the area (Fig. 120).

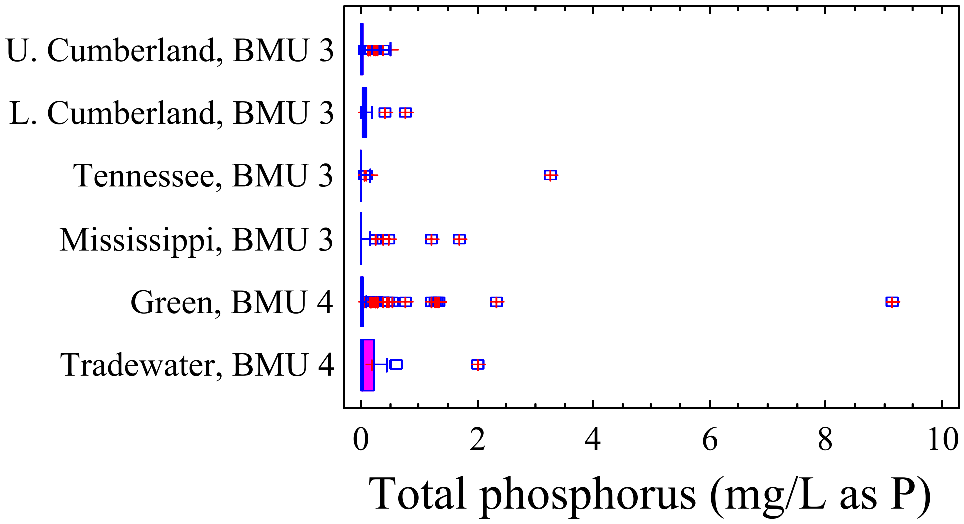


Figure 119. Summary of total phosphorus measurements grouped by major watershed. One value greater than 10 mg/L was excluded for clarity. DOW = 0.1 mg/L.

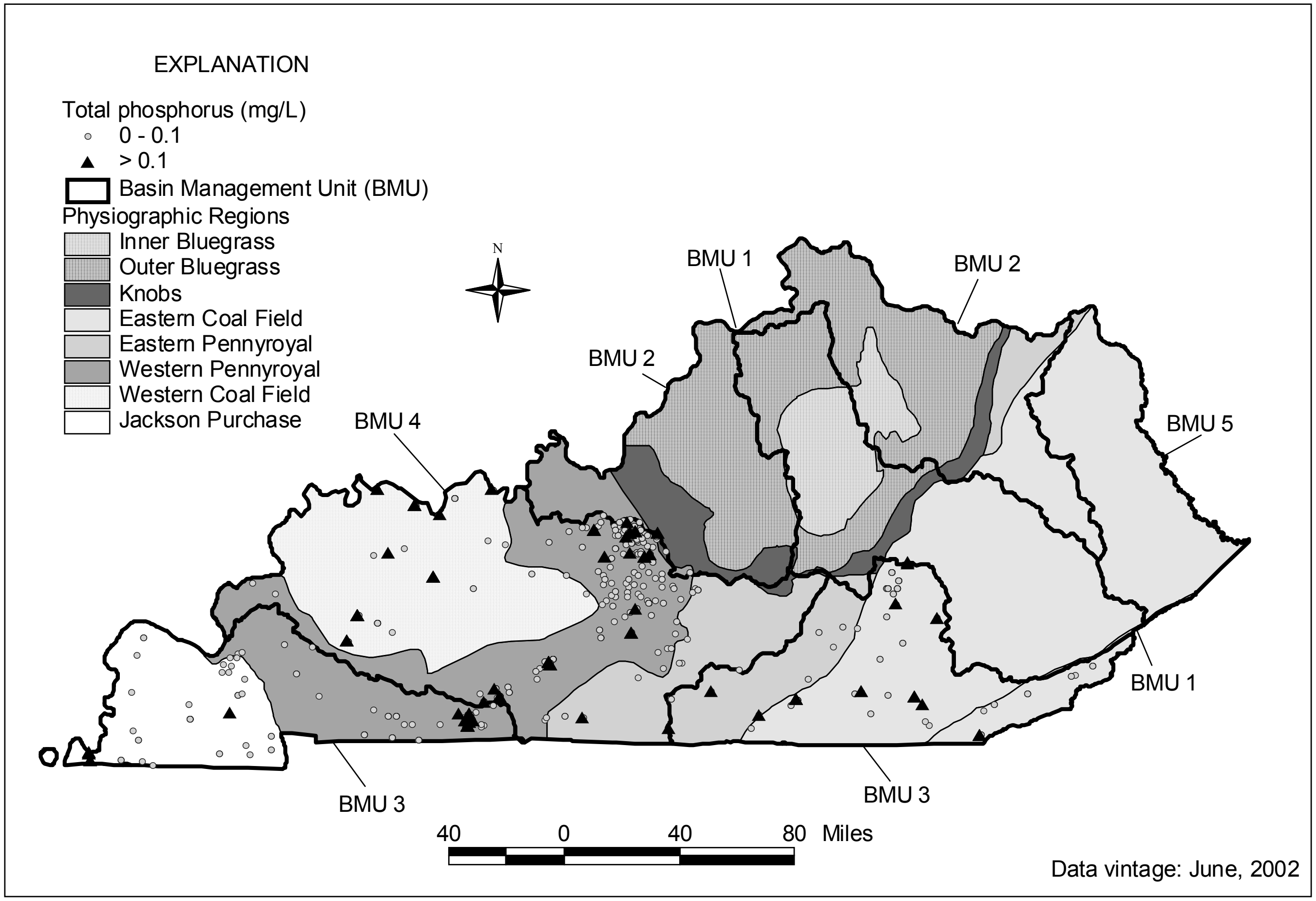


Figure 120. Map showing sample sites and total phosphorus values. Superimposed symbols indicate that values measured at the same site but at different sampling times fell into different ranges.

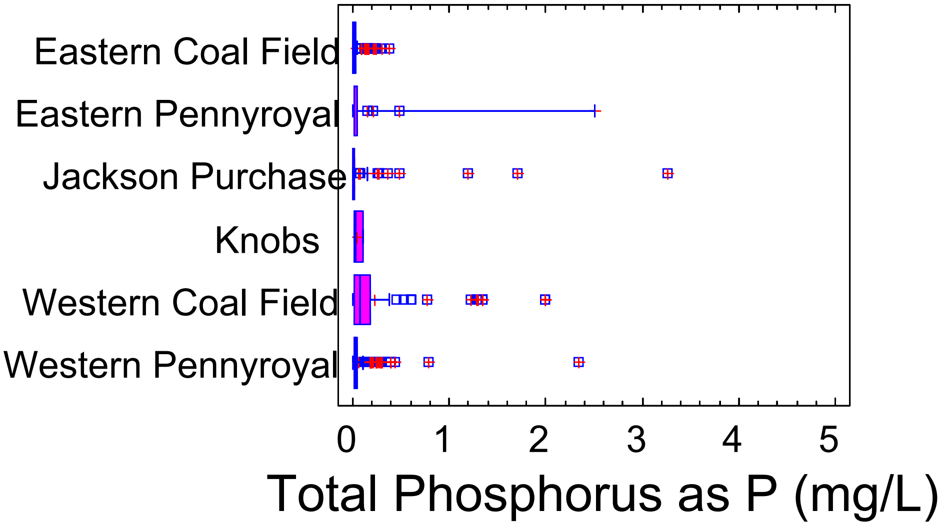


Figure 121. Total phosphorus measurements grouped by physiographic region. Values greater than 5 mg/L were omitted for clarity. DOW = 0.1 mg/L.

High concentrations are more common in wells than in springs (Fig. 122), and more common in shallow wells than in deep wells (Fig. 123).

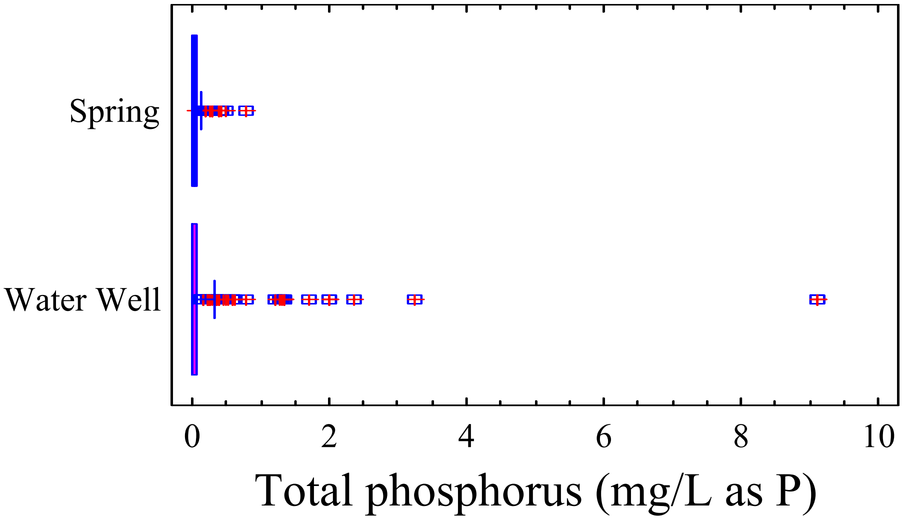


Figure 122. Summary of total phosphorus measurements grouped by site type. DOW = 0.1 mg/L.

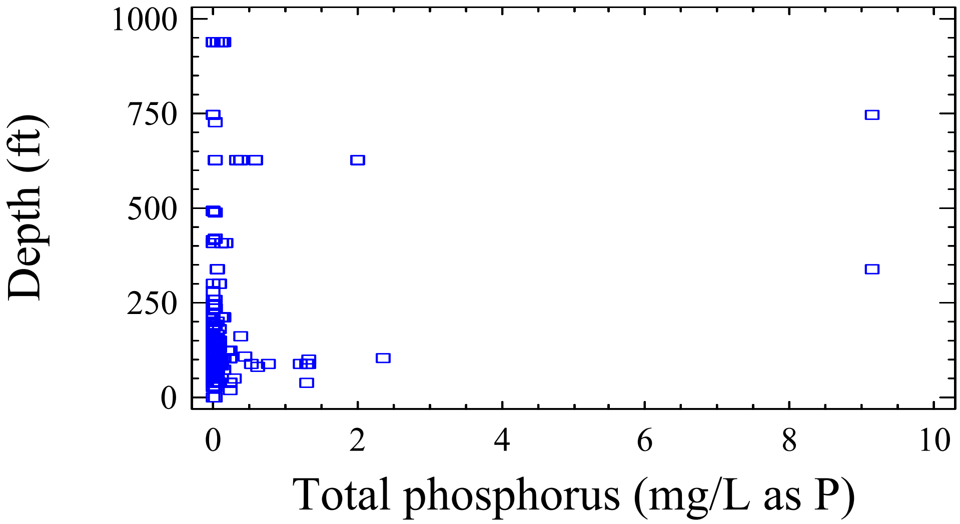


Figure 123. Plot of total phosphorus concentrations versus well depth. DOW = 0.1 mg/L.

Summary: Total phosphorus concentrations that exceed the recommended value of 0.1 mg/L as phosphorus were reported throughout BMU's 3 and 4. Relatively few sites in the Eastern Coal Field, Western Coal Field, or the Jackson Purchase yield groundwater with high total phosphorus; such sites are more common in the Western Pennyroyal Region. 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. However, the observation that shallow wells are most likely to produce groundwater having high phosphorus concentrations suggests there may be an NPS contribution.

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 (USGS, 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 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, it is important to quantify the existence of any detectable pesticides in Kentucky groundwater.

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 at 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 used 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 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 1,050 2,4-D measurements from 167 sites (Table 23). In BMU 3, 510 of 516 measurements (98.8 percent) were reported as less than a detection limit; in BMU 4, 525 of 534 measurements (98.3 percent) were reported as less than a detection limit. No site yielded groundwater with 2,4-D concentrations above the MCL. Only seven sites had detectable levels of 2,4-D (Fig. 124). Five of the seven sites where 2,4-D was detected are in the Western Pennyroyal Region, in either the Green River or Lower Cumberland River watersheds. 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 measurements (mg/L).

	BMU 3	**BMU 4**
Analyses	516	534
Sites	117	50
Maximum	< 0.0009	0.0021
3rd Quartile	< 0.000335	< 0.0001
Median	< 0.0001	< 0.0001
1st Quartile	< 0.0001	< 0.0001
Minimum	0.00001	< 0.000005
Sites where MCL exceeded	0	0
Sites where detected	3	4

MCL = 0.07 mg/L

Summary: The pesticide 2,4-D was detected at 7 of 167 sites; all detections were in groundwater from springs. No samples had 2,4-D concentrations greater than the MCL value of 0.07 mg/L. The observed occurrences, coupled with the short half-life, suggests that 2,4-D degrades in the time it takes to travel from application site to water wells. However, rapid runoff can transport 2,4-D to springs, where it could be consumed or used for other domestic purposes.

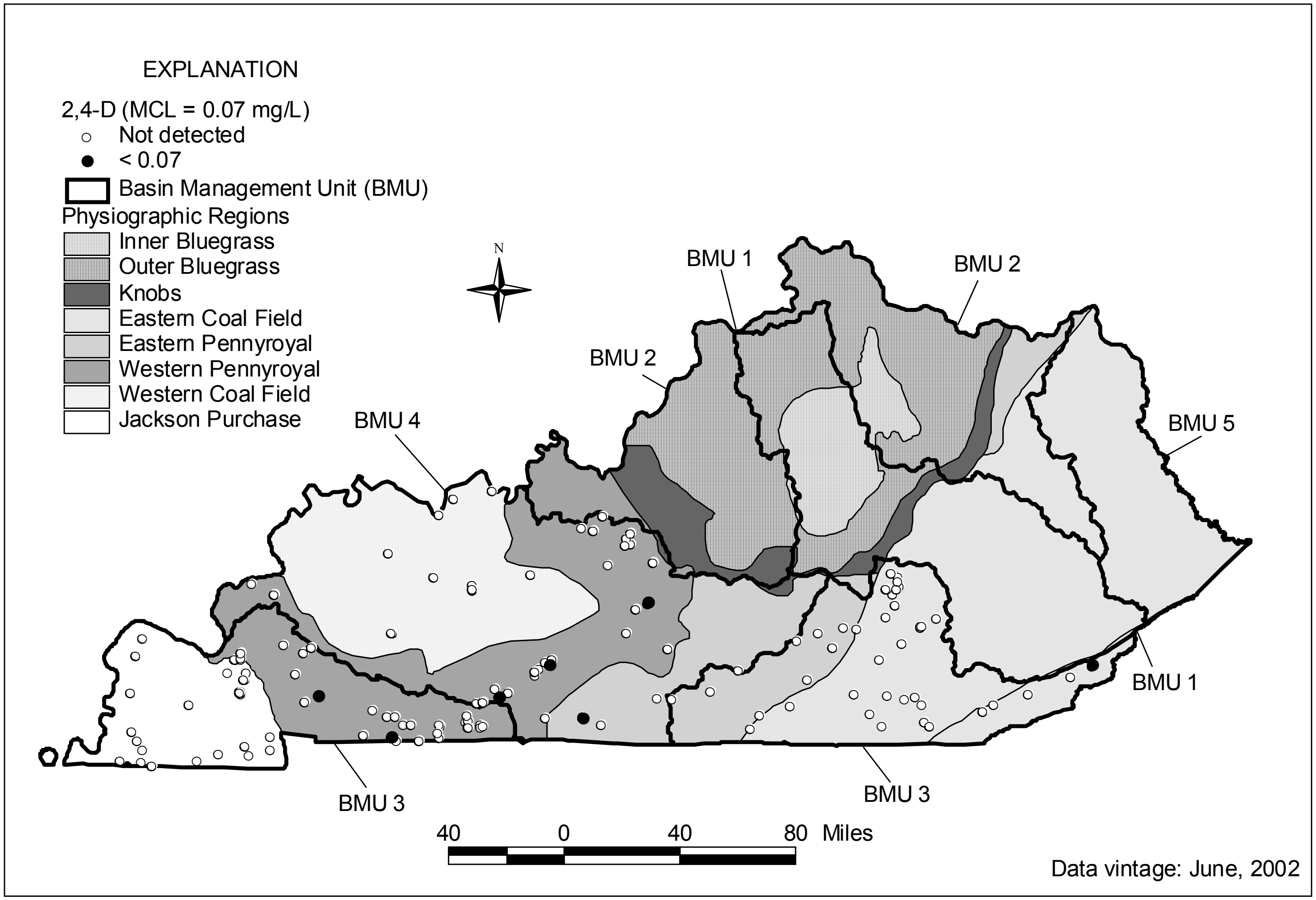


Figure 124. Location of sites where 2,4 D was measured. No sites exceeded the MCL.

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 due to 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 3,095 results of analyses from 172 sites (Table 24). More than 60 percent of the sites and more than 77 percent of the measurements were from BMU 3, and 1,078 of the 2,413 measurements from BMU 3 were reported from a single site. In BMU 3, 1,543 of 2,413 measurements (63.9 percent) were reported as less than a detection limit; in BMU 4, 653 of 682 measurements (95.7 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.

Table 24. Summary of alachlor measurements (mg/L).

Pesticide	BMU 3	BMU 4
Analyses	2,413	682
Sites	107	65
Maximum	0.01200	0.00064
3rd Quartile	0.00010	< 0.00006
Median	< 0.00006	< 0.00005
1st Quartile	< 0.00006	< 0.00004
Minimum	< 0.00002	< 0.00001
Sites > MCL	2	0
Sites where detected	20	10

MCL = 0.002 mg/L

Two sites in the Lower Cumberland River watershed, Western Pennyroyal Region of BMU 3, yielded groundwater with alachlor concentrations above the MCL (Fig. 125). Thirty sites, most of them in the Lower Cumberland River watershed, Western Pennyroyal Region of BMU 3, had detectable levels of alachlor.

Only four 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 springs rather than wells (Fig. 126). 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.

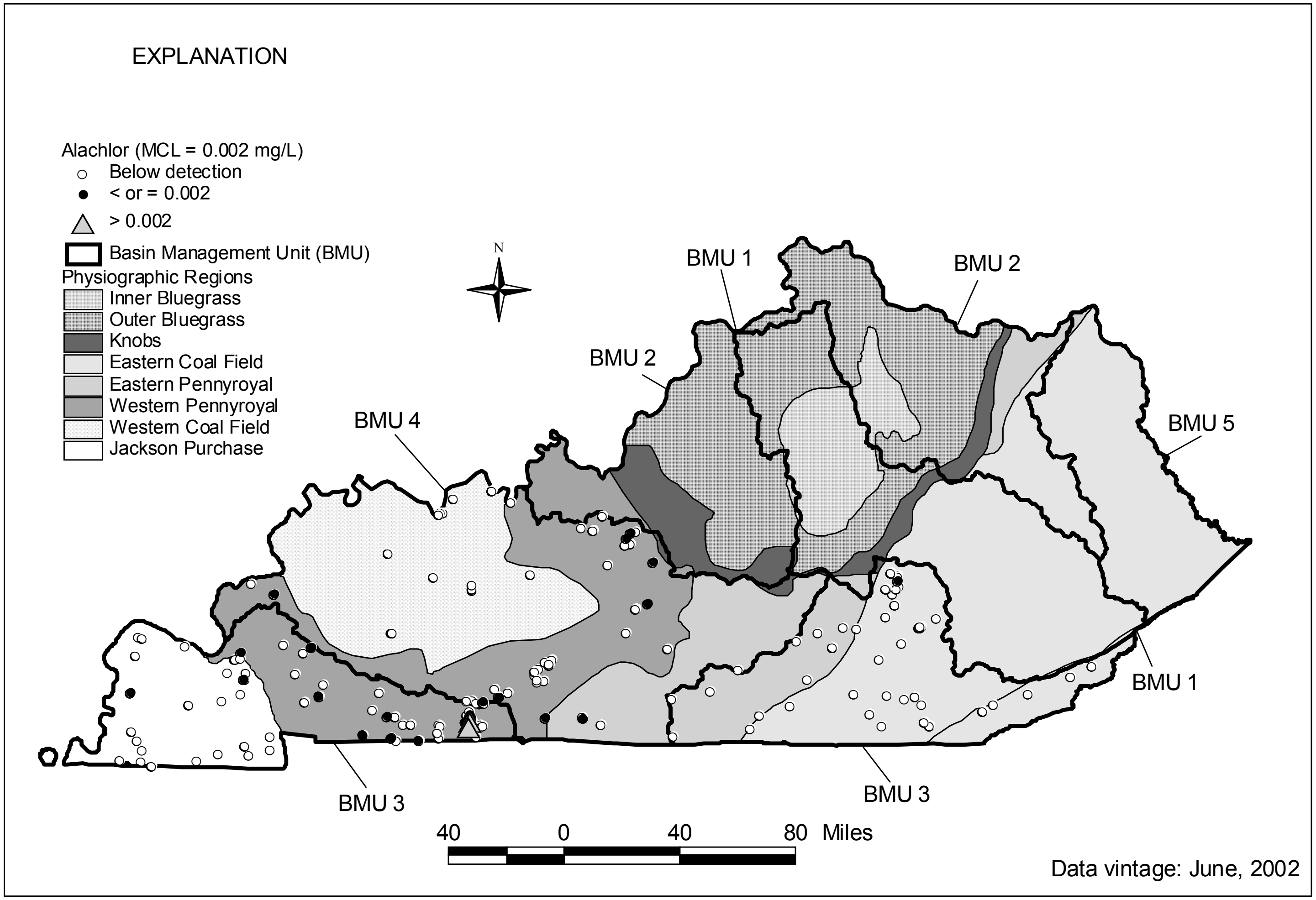


Figure 125. Location of sites where alachlor was measured.

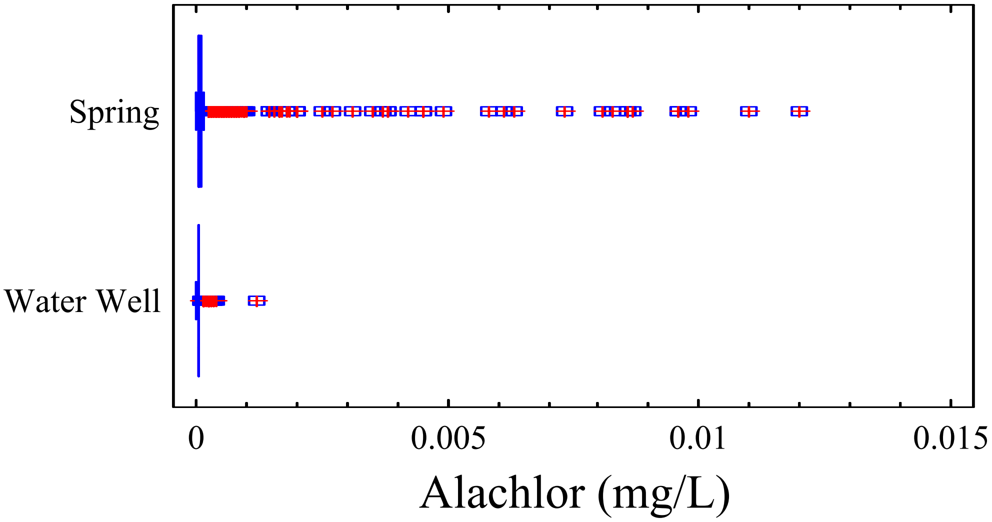


Figure 126. Summary of alachlor measurements grouped by site type. MCL = 0.002 mg/L.

Summary: Alachlor exceeded the MCL at two sites. It was detected at 30 of 172 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.

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 1,360 analytical reports of atrazine from 120 sites (Table 25). In BMU 3, 400 of 638 measurements were reported as less than a detection limit; in BMU 4, 497 of 722 measurements were reported as less than a detection limit. Atrazine concentrations were above analytical detection limits at 21 sites in BMU 3 and 24 sites in BMU 4. Atrazine concentrations exceeded the MCL at four sites in BMU 3 and three sites in BMU 4.

Table 25. Summary of atrazine measurements (mg/L).

Atrazine	**BMU 3**	**BMU 4**
Analyses	638	722
Sites	62	58
Maximum	0.039	0.00946
3rd Quartile	0.00042	< 0.0003
Median	< 0.0003	< 0.0002
1st Quartile	0.00006	< 0.00005
Minimum	0.00002	0.00000
Sites where MCL exceeded	4	3
Sites where detected	21	24

MCL = 0.003 mg/L

Figure 127 shows that atrazine detections and sites where the MCL was exceeded are mostly in the Western Pennyroyal Region, in watersheds of the Green and Lower Cumberland Rivers.

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. 128). 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. 129).

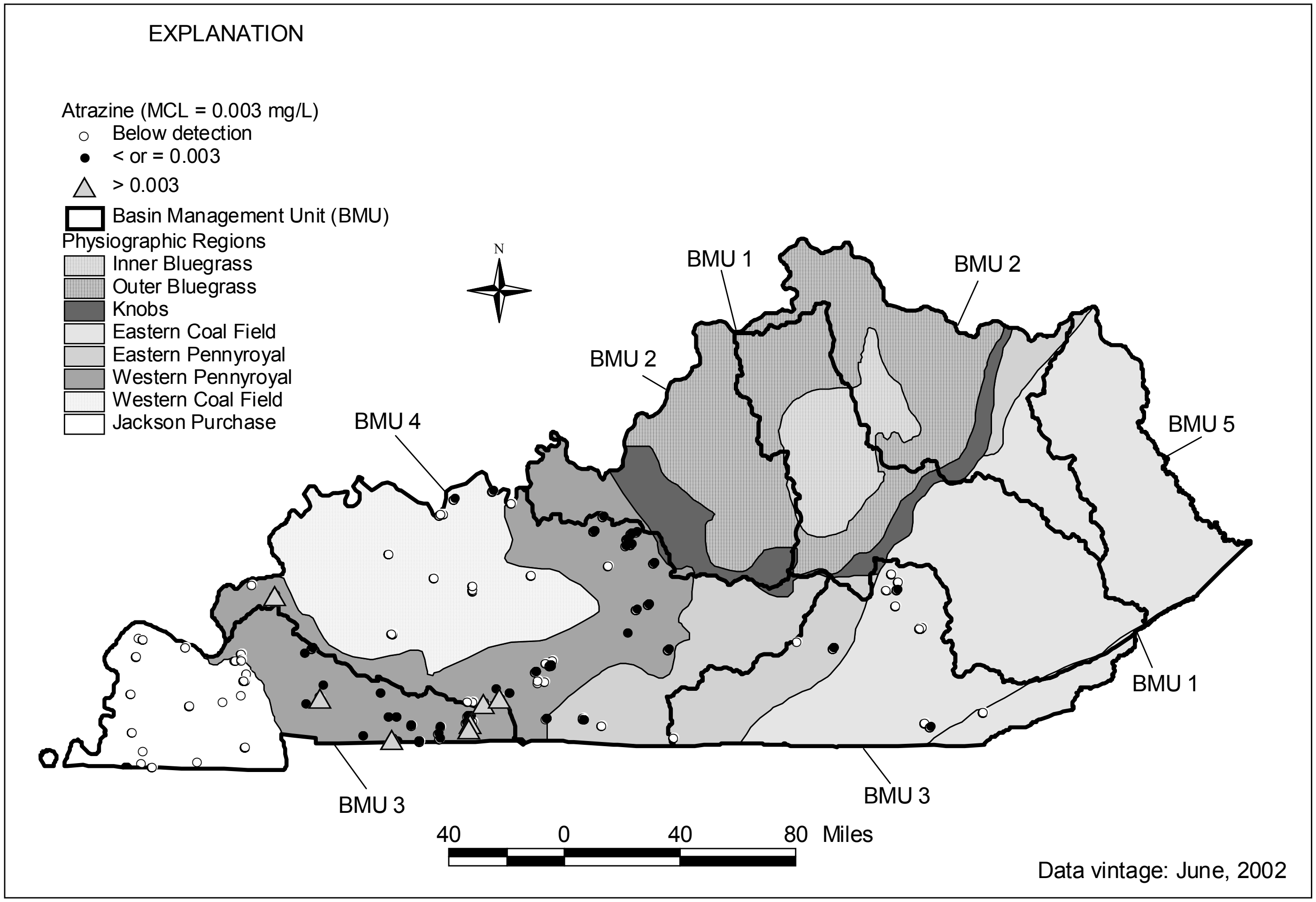


Figure 127. Location of sites where atrazine was measured.

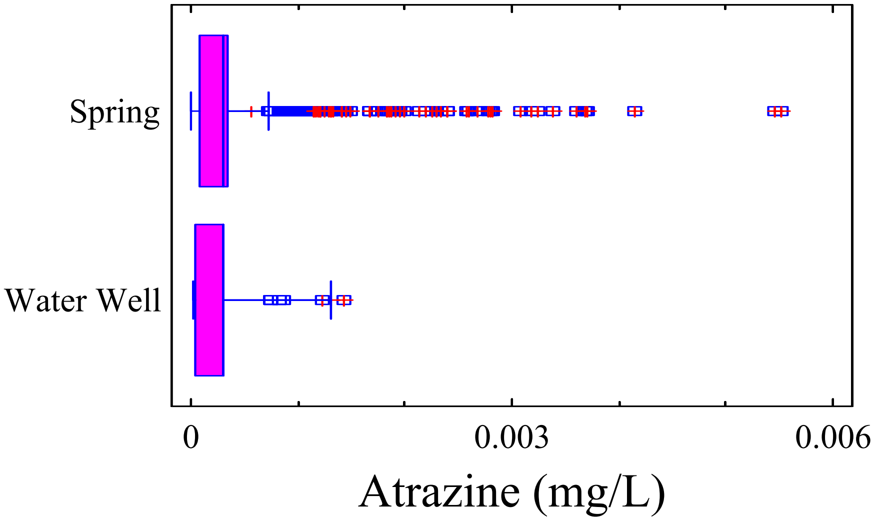


Figure 128. Summary of atrazine measurements grouped by site type. MCL = 0.003 mg/L.

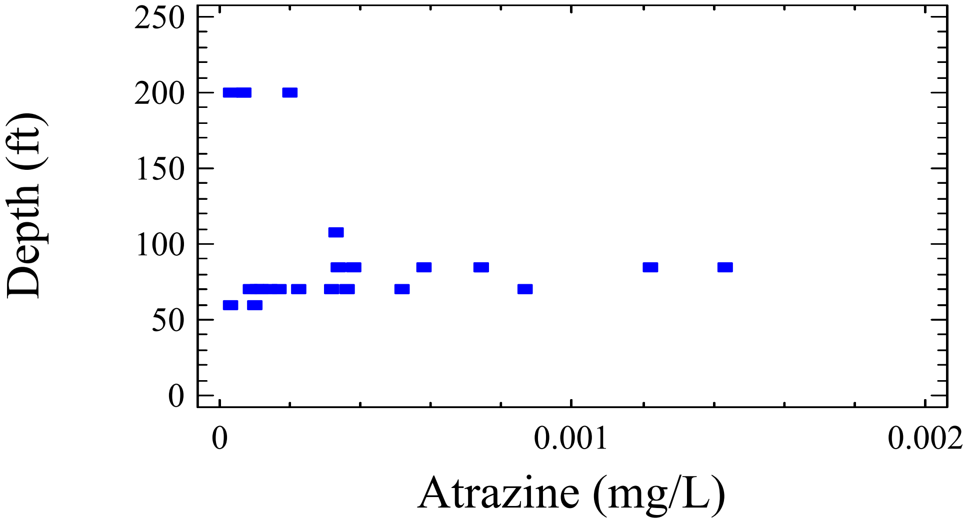


Figure 129. Plot of atrazine concentrations versus well depth. Only results that exceeded analytical detection limits are shown. MCL = 0.003 mg/L.

Summary: Seven sites in the project area produced groundwater that exceeded the MCL for atrazine; 45 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. However, rapid runoff from fields to springs allows high atrazine concentrations to contaminate springs.

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. DOW has set a health advisory limit (HAL) of 0.001 mg/L.

The data repository contained 935 reports of cyanazine analyses at 154 sites (Table 26). Four measurements in BMU 3 and no measurements in BMU 4 exceeded analytical detection limits. Groundwater from springs in the Lower Cumberland River watershed, Western Pennyroyal Region, accounted for all the samples in which cyanazine was present at detectable concentrations (Fig. 130). One spring in BMU 3 and no sites in BMU 4 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 measurements (mg/L).

Pesticide	BMU 3	BMU 4
Analyses	489	446
Sites	97	57
Maximum	0.00440	< 0.0001
3rd Quartile	< 0.00010	< 0.0001
Median	< 0.00005	< 0.00005
1st Quartile	< 0.00004	< 0.00004
Minimum	< 0.00004	< 0.00004
Sites where HAL exceeded	1	0
Sites where detected	3	0

HAL = 0.001 mg/L

Summary: Cyanazine rarely persists at detectable levels in the project area. The highest concentrations were observed in springs in the Lower Cumberland River watershed of the Western Pennyroyal physiographic region.

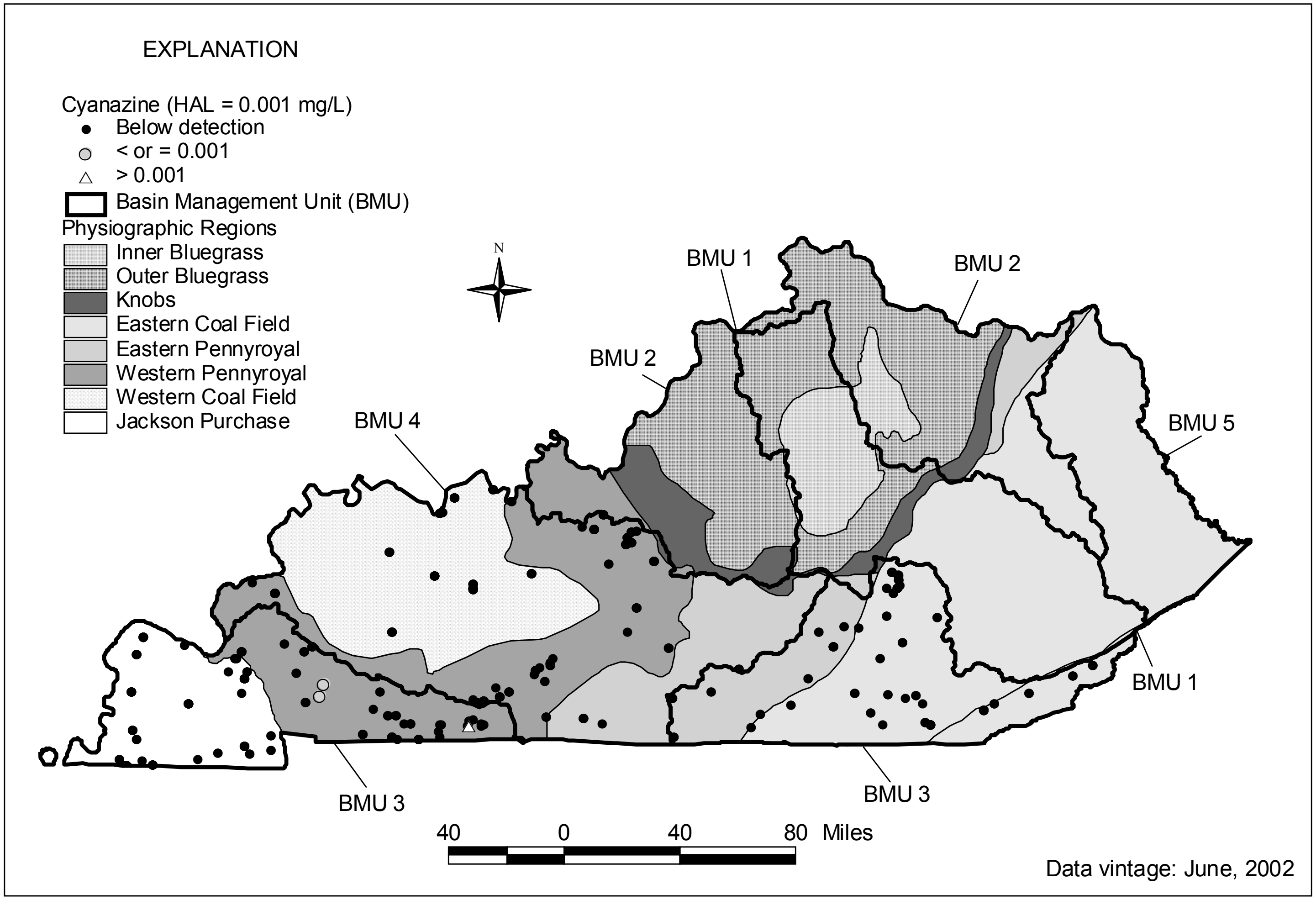


Figure 130. Location of sites where cyanazine was measured.

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 half-lives of 15 to 70 days, and is highly persistent in water. There is no MCL for metolachlor; DOW has set a health advisory limit (HAL) of 0.1 mg/L.

The data repository contained 3,306 metolachlor measurements from 166 sites (Table 27). Most measurements were below analytical detection (1,247 of 2,650 in BMU 3 and 556 of 656 in BMU 4). No sites produced groundwater that exceeded the HAL for metolachlor. Thirty-one sites in BMU 3 and 15 sites in BMU 4 produced water that had metolachlor concentrations above the analytical detection limit. Most of these sites were in the Western Pennyroyal Region, Lower Cumberland River watershed, of BMU 3 (Fig. 131).

Table 27. Summary of metalochlor measurements (mg/L).

	BMU 3	**BMU 4**
Analyses	2,650	656
Sites	100	66
Maximum	0.0296	0.00468
3rd Quartile	0.00039	< 0.0002
Median	0.00011	< 0.00005
1st Quartile	< 0.00008	< 0.00005
Minimum	0.000001	0.000001
Sites where HAL exceeded	0	0
Sites where detected	31	15

HAL = 0.1 mg/L

The highest metolachlor concentrations were observed in groundwater from springs (Fig. 132). Metolachlor has been detected in wells as deep as about 200 ft (Figure 133).

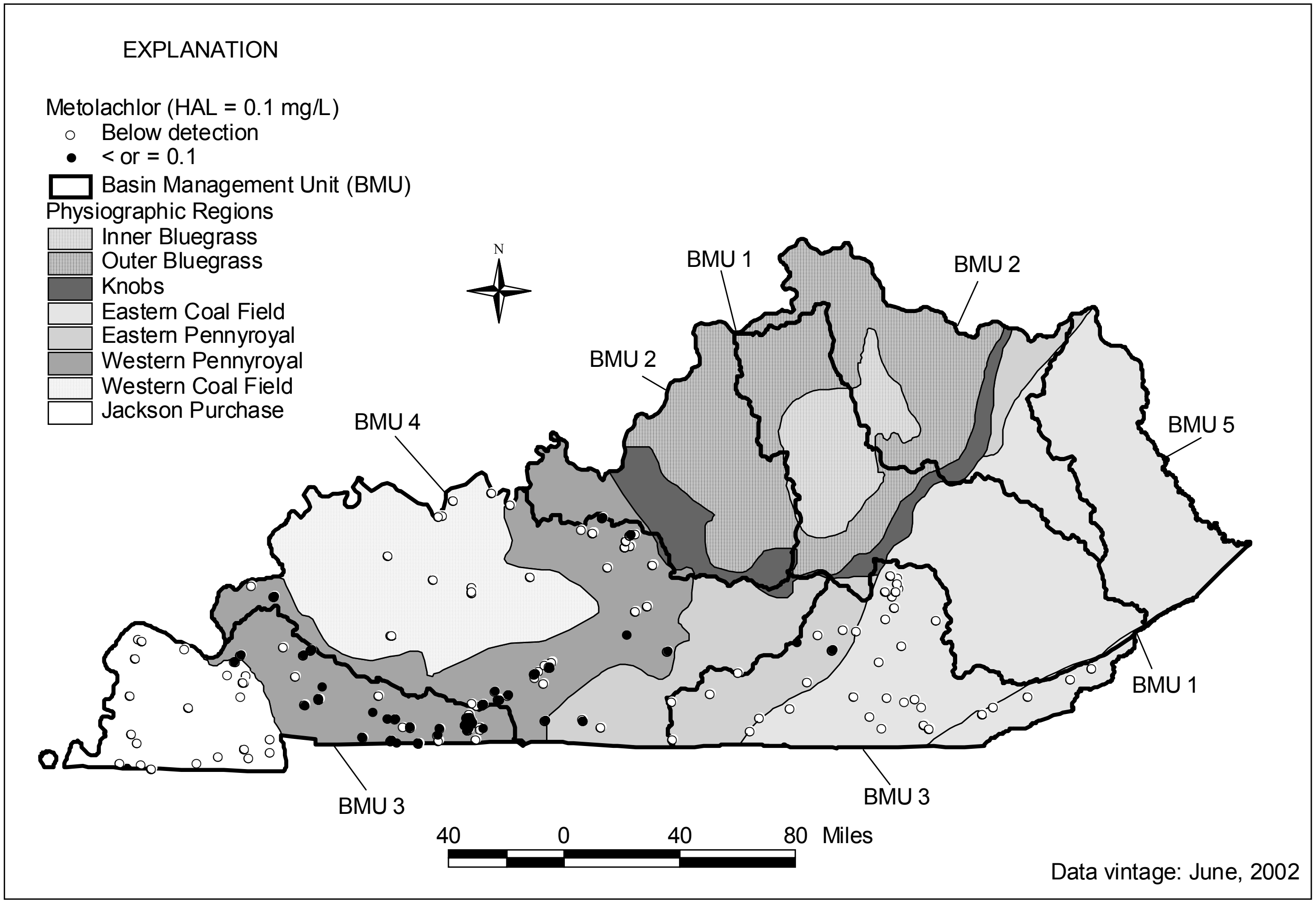


Figure 131. Location of sites where metolachlor was measured.

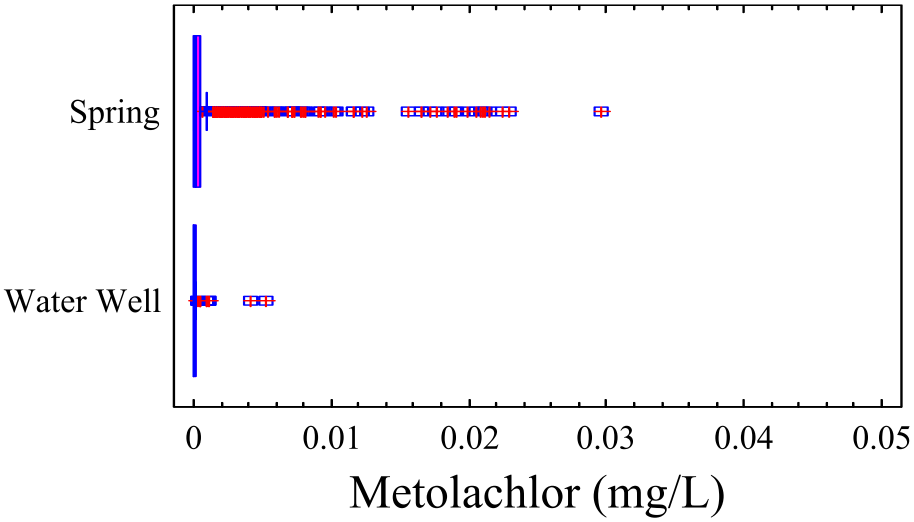


Figure 132. Summary of metolachlor measurements by site type. HAL = 0.1 mg/L.

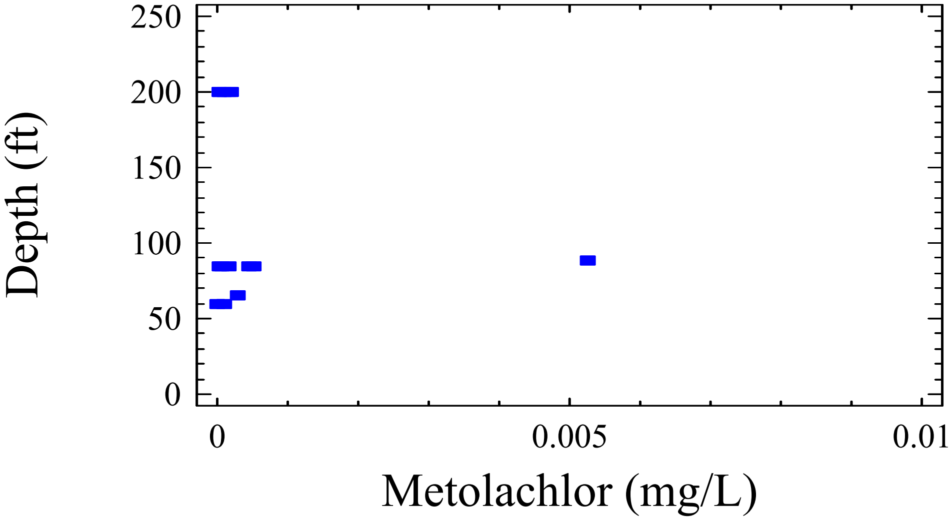


Figure 133. Plot of metolachlor concentrations versus well depth. Only values greater than analytical detection limits are shown. HAL = 0.1 mg/L.

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.

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 EPA MCL for simazine is 0.004 mg/L.

The data repository contained 1,404 simazine measurements from 164 sites (Table 28). Most measurements (658 of 690 in BMU 3, 672 of 714 in BMU 4) were below analytical detection limits. Sixty-four of the 74 measurements that were above analytical detection limits were in groundwater from springs; only 10 of the 74 were in groundwater from wells. Fifteen sites in BMU 3 and 12 sites in BMU 4 yielded groundwater with detectable quantities of simazine (Fig. 134). The simazine concentration in groundwater exceeded the MCL at one site in the Lower Cumberland River watershed, Western Pennyroyal Region, of BMU 3 (Fig. 134). 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 measurements (mg/L).

	BMU 3	**BMU 4**
Analyses	690	714
Sites	99	65
Maximum	0.0045	0.002043
3rd Quartile	< 0.0003	< 0.0003
Median	< 0.0001	< 0.000051
1st Quartile	< 0.00004	< 0.0005
Minimum	< 0.00002	0.000011
Sites where MCL exceeded	1	0
Sites where detected	15	12

MCL = 0.004 mg/L

Summary: Simazine concentrations exceeded the MCL at one site and were detected at 27 of 164 sites. Only six of the sites where simazine was detected are water wells; the other 21 are springs. These observations suggest that rapid transport can carry simazine to springs more readily than to water wells.

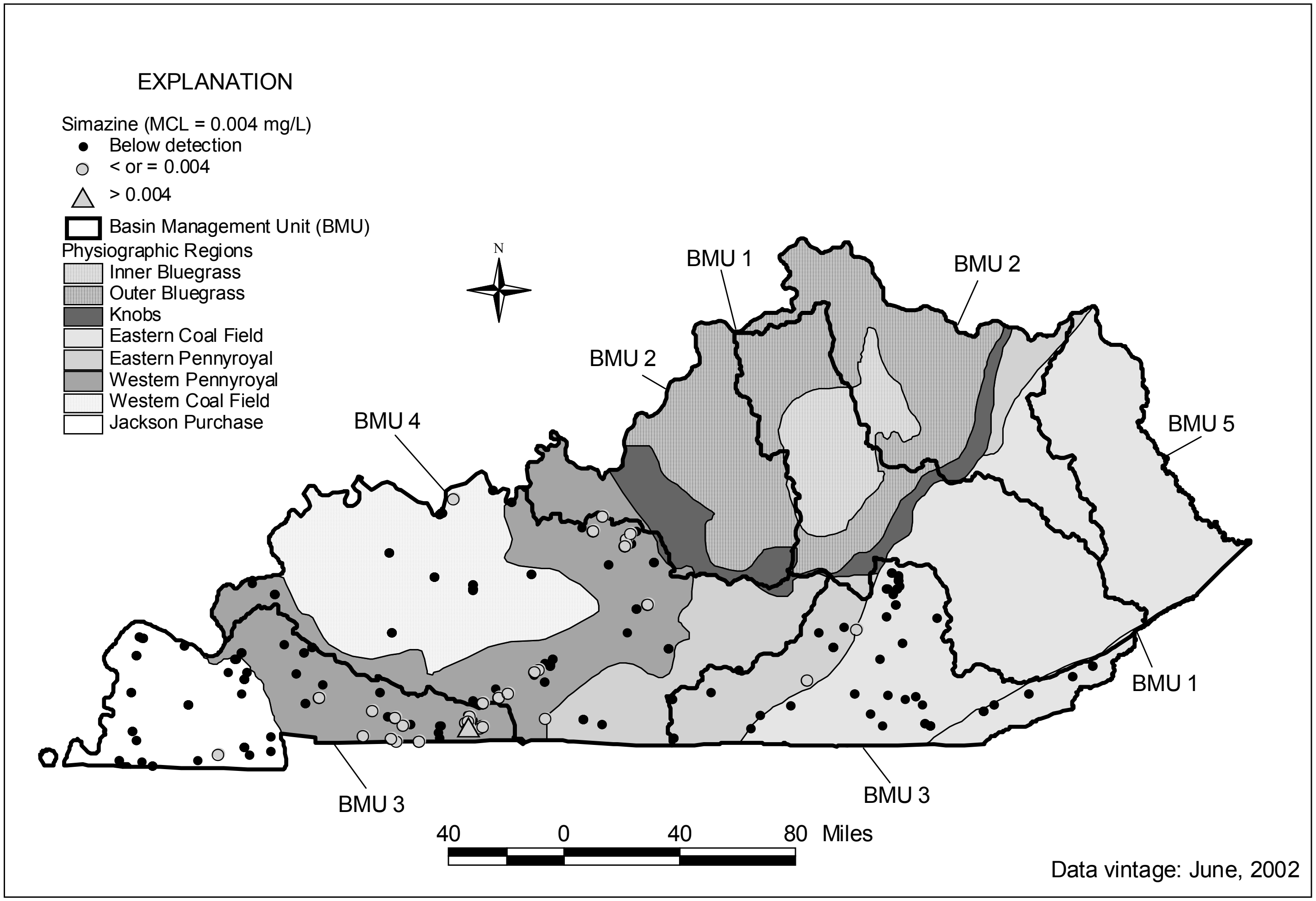


Figure 134. Location of sites where simazine was measured.

Volatile Organic Compounds

The volatile organic compounds (VOC's) benzene, ethylbenzene, toluene, and xylenes 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. Natural sources such as crude oil seeps are rare. Any detected amounts of these refined volatile organic chemicals most likely 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 reports of "<0.02 mg/L" at one time and "0.01 mg/L" at another sampling event, the maximum value recorded would be 0.01 mg/L.

Records from monitoring wells (identified by an AKGWA number that begins with "8"; e.g., 80001234) were excluded to avoid any wells drilled to test for leaking underground storage tank contamination. In the following discussions, summaries of potential sources and health effects of the selected pesticides were taken from the U.S. 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 709 benzene measurements at 346 sites in BMU's 3 and 4 (Table 29). Fifty-three measurements were above analytical detection limits.

Table 29. Summary of benzene measurements (mg/L).

	BMU 3	**BMU 4**
Measurements	425	284
Measurements above analytical detection limit	15	38
Sites	224	122
Sites above analytical detection limits	10	21
Sites above MCL	2	4
Maximum	0.01	2.36
3rd quartile	< 0.001	0.001
Median	< 0.0005	< 0.0005
1st quartile	< 0.0005	< 0.0005
Minimum	< 0.0005	0.00038

MCL = 0.005 mg/L
"<" indicates that the analysis result was less than the detection limit; the value of the detection limit follows the "<" symbol.

Benzene was detected at 31 sites, mostly in the Western Pennyroyal Region, Lower Cumberland and Green River watersheds (Fig. 135). Benzene concentrations exceeded the MCL at three wells and three springs.

The highest benzene concentrations were found in springs (Fig. 136). No relation between benzene concentration and well depth was observed; however, most samples were taken from springs, and few sampled wells had a depth recorded. The deepest well at which benzene was found at levels above analytical detection was 185 ft deep.

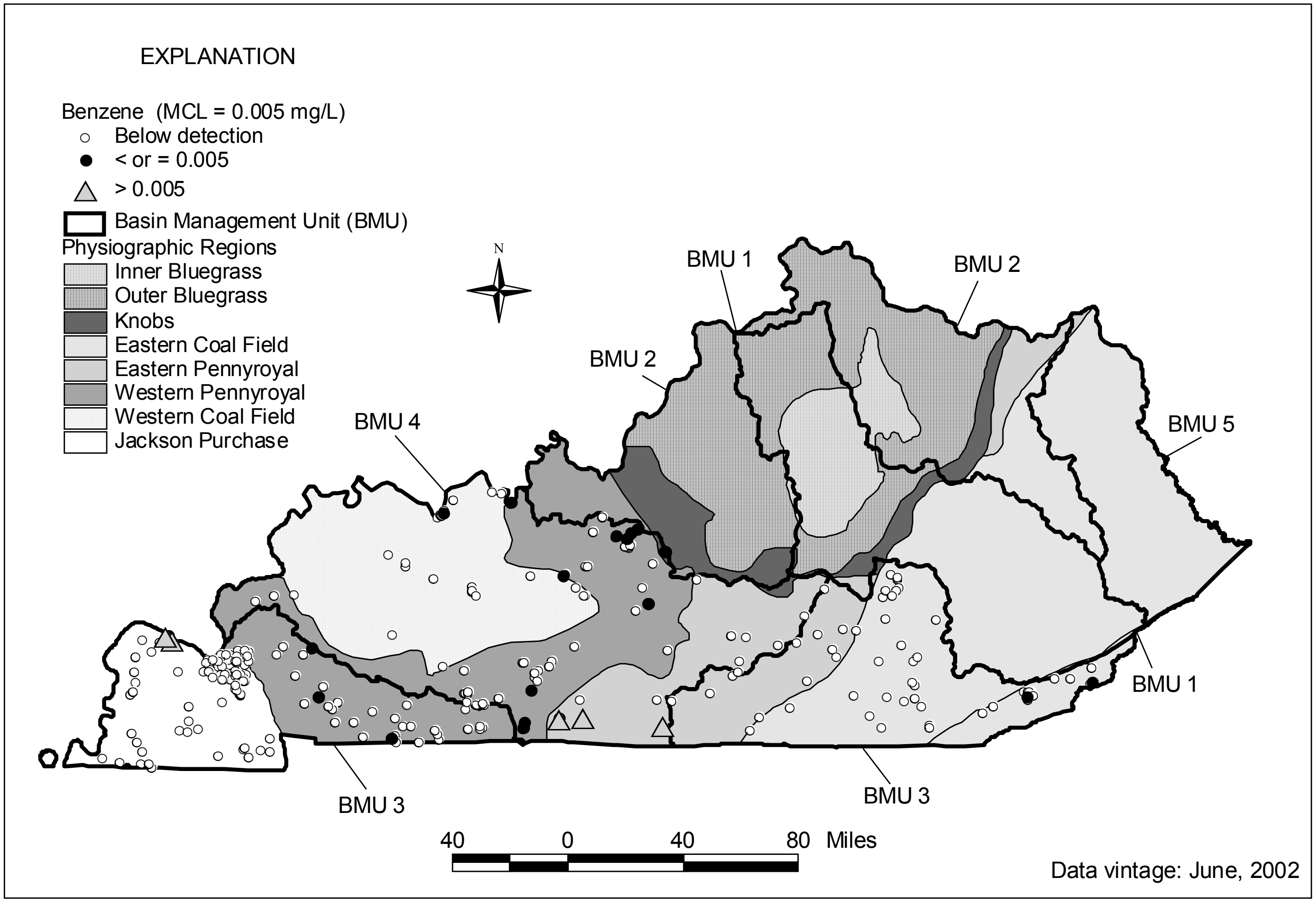


Figure 135. Map showing sample sites and benzene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

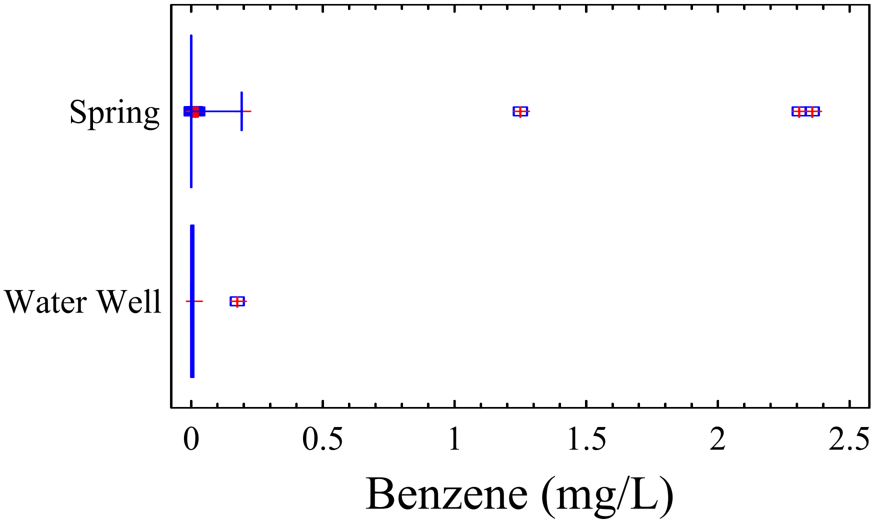


Figure 136. Summary of benzene measurements grouped by site type. Only values greater than analytical detection limits are shown. MCL = 0.005 mg/L.

Summary: Occurrences of detectable benzene in groundwater are rare in the project area. Sites where benzene was detected are predominantly in the karst terrane of the Western Pennyroyal Region. Springs are more susceptible to benzene contamination than wells; however, benzene was detected in a well that is 185 ft deep.

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. EPA has set an MCL for ethylbenzene of 0.7 mg/L.

The data repository contained 708 ethylbenzene measurements at 346 sites (Table 30). Only about 6 percent of the analytical results were greater than the analytical detection limits. Ethylbenzene concentrations exceeded analytical detection limits at 25 of 346 sites. These sites were either springs, shallow (< 65 ft) wells, or wells where no depth was recorded. Ethylbenzene exceeded the MCL at one spring and at one 60-ft-deep well. Both sites where the MCL was exceeded are in the karst terrane of the Eastern Pennyroyal Region, Green River watershed, BMU 4 (Fig. 137).

Table 30. Summary of ethylbenzene measurements (mg/L).

	BMU 3	**BMU 4**
Measurements	425	283
Measurements above analytical detection limits	13	29
Sites	224	122
Sites above analytical detection limits	8	17
Sites above MCL	0	2
Maximum	0.0706	7.08
3rd quartile	< 0.001	< 0.0005
Median	< 0.0005	< 0.0005
1st quartile	< 0.0005	< 0.0005
Minimum	< 0.0005	< 0.0005

MCL = 0.7 mg/L

"<" indicates that the analysis result was less than the detection limit; the value of the detection limit follows the "<" symbol.

Summary: Detectable levels of ethylbenzene in groundwater are rare in the project area. Springs are more susceptible to ethylbenzene contamination than wells, and shallow wells are more susceptible than intermediate or deep wells. Ethylbenzene was detected in a well that is 60 ft deep. Ethylbenzene was detected most frequently at sites in the karst terrane of the Western Pennyroyal Region. However, the sites where ethylbenzene exceeded the MCL are in the karstic Eastern Pennyroyal Region in the Green River watershed.

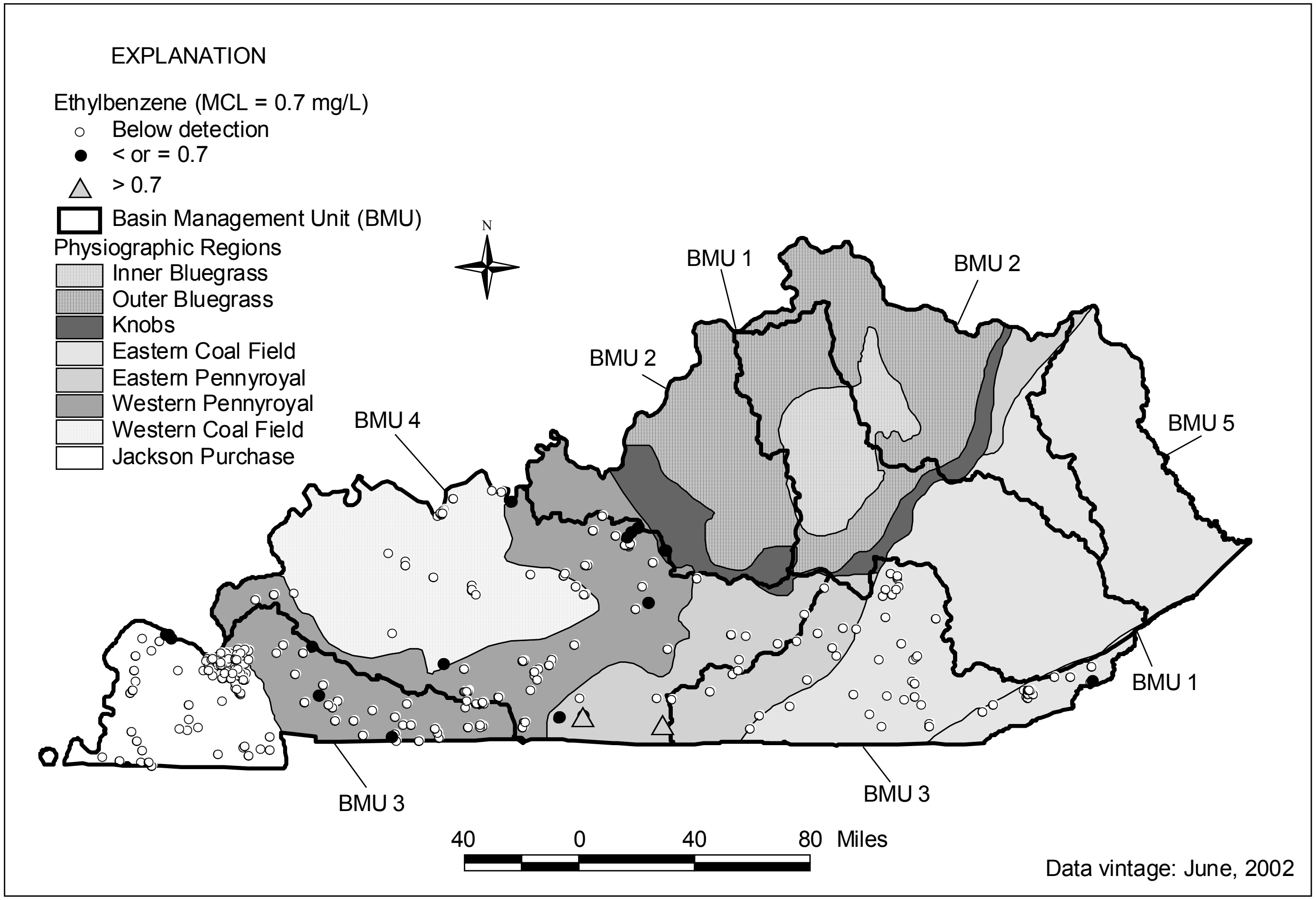


Figure 137. Map showing sample sites and ethylbenzene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

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 EPA MCL for toluene is 1.0 mg/L.

The data repository contained 709 toluene measurements at 346 sites in the project area (Table 31). Fifteen measured concentrations in BMU 3 and 34 measurements in BMU 4 were above analytical detection limits. Toluene concentrations exceeded analytical detection limits at 12 springs and 16 wells. No systematic relation of toluene concentrations and well depth was found. Of the wells where toluene was detected, two were deeper than 200 ft, nine had no depth recorded, and five were less than 80 ft deep. Most of the wells and springs where toluene was detected in groundwater are in the karstic Western Pennyroyal Region (Fig. 138). Toluene concentrations exceeded the MCL at two springs and one well in the Eastern Pennyroyal karstic terrane of the Green River watershed in BMU 4 (Fig. 138).

Table 31. Summary of toluene measurements (mg/L).

	BMU 3	BMU 4
Measurements	426	283
Measurements above analytical detection limits	15	34
Sites	224	122
Sites above analytical detection limits	10	18
Sites above MCL	0	3
Maximum	0.0100	4.02
3rd quartile	< 0.001	0.001
Median	< 0.0005	< 0.0005
1st quartile	< 0.0005	< 0.0005
Minimum	< 0.0005	< 0.0005

MCL = 1.0 mg/L
"<" indicates that the analysis result was less than the detection limit; the value of the detection limit follows the "<" symbol.

Summary: Like the other volatile organic chemicals, toluene has been detected in groundwater in the project area. Detectable concentrations and toluene levels above the MCL are most likely to be found in springs and shallow wells in the carbonate karst terrane of the Eastern and Western Pennyroyal Regions. Toluene has entered the intermediate groundwater system, as evidenced by a detectable concentration in a 265-ft-deep well.

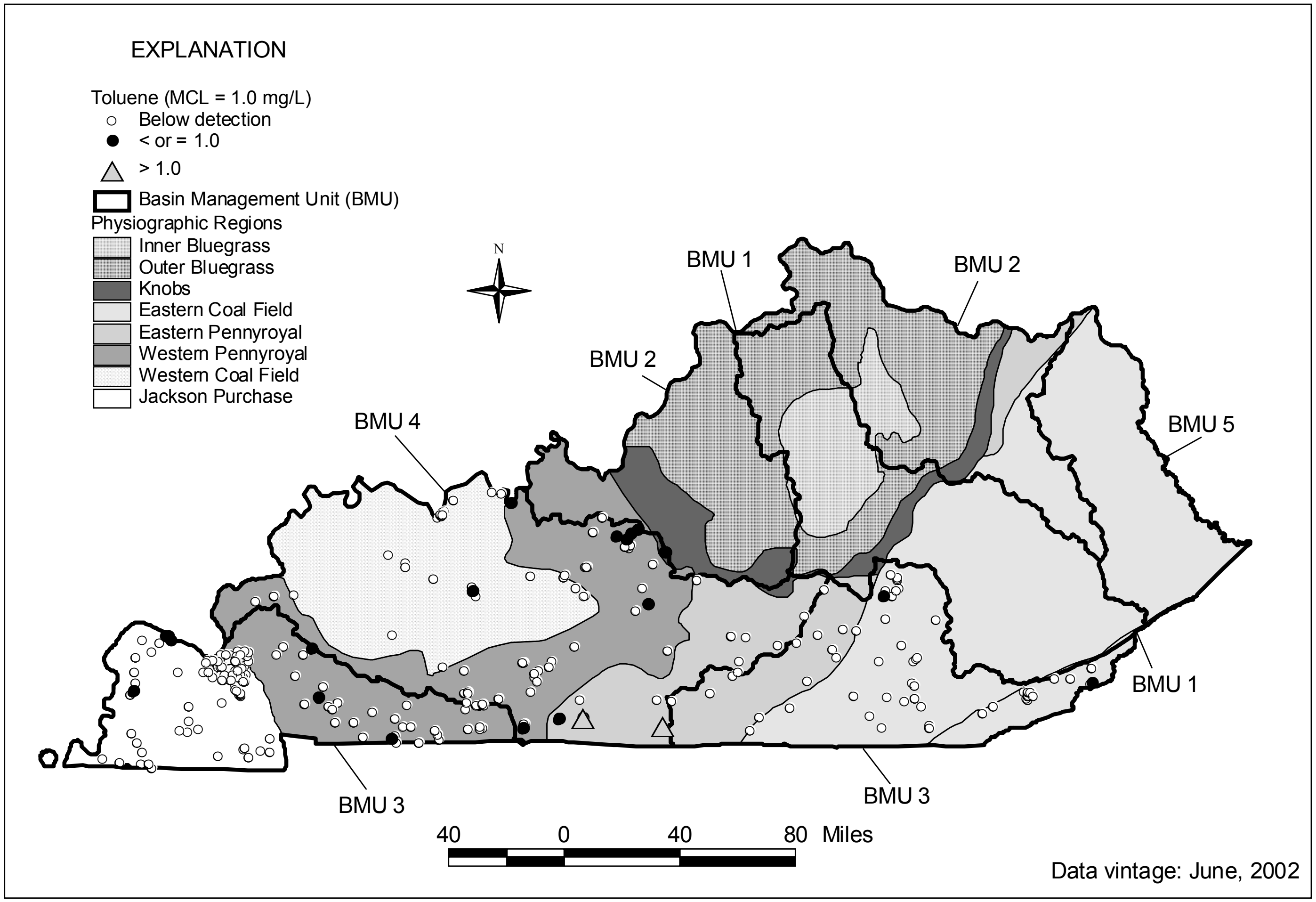


Figure 138. Map showing sample sites and toluene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

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 EPA MCL is 10 mg/L for the sum of O-Xylene, P-Xylene, and M-Xylene.

The data repository contains 1,285 such measurements at 339 sites in BMU's 3 and 4 (Table 32). Xylene analyses in the data repository are reported as "1,3-Xylene & 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 it necessary to calculate "total xylenes" at each site for a given sample collection event.

Forty-eight laboratory measurements for xylenes were above analytical detection limits. Twenty-two sites, mostly in the karstic Eastern and Western Pennyroyal Regions, had xylene concentrations greater than the analytical detection limit (Fig. 139). Of these 22 sites, 13 were springs, six were wells less than 780 ft deep, and three were wells with no depth recorded. One shallow well (59 ft deep) in the Eastern Pennyroyal Region of BMU 4 had a total xylene concentration that exceeded the MCL (Fig. 139). The deepest well at which xylene was detected is 80 ft.

Table 32. Summary of total xylene measurements (mg/L)

	BMU 3	**BMU 4**
Measurements	872	413
Measurements above analytical detection limits	19	29
Sites	223	116
Sites above analytical detection limits	9	13
Sites above MCL	0	1
Maximum	< 0.5	24.8
3rd quartile	< 0.001	< 0.0005
Median	< 0.0005	< 0.0005
1st quartile	< 0.0005	< 0.0005
Minimum	0.000275	< 0.0005

MCL = 10.0 mg/L

"<" indicates that the analysis result was less than the detection limit; the value of the detection limit follows the "<" symbol.

Summary: Few sampled sites had total xylene concentrations that were above analytical detection limits. Shallow wells and springs in the karst terrane of the Eastern and Western Pennyroyal Regions are more likely to have detectable xylene levels than are wells or springs in the coal fields or the Jackson Purchase Region.

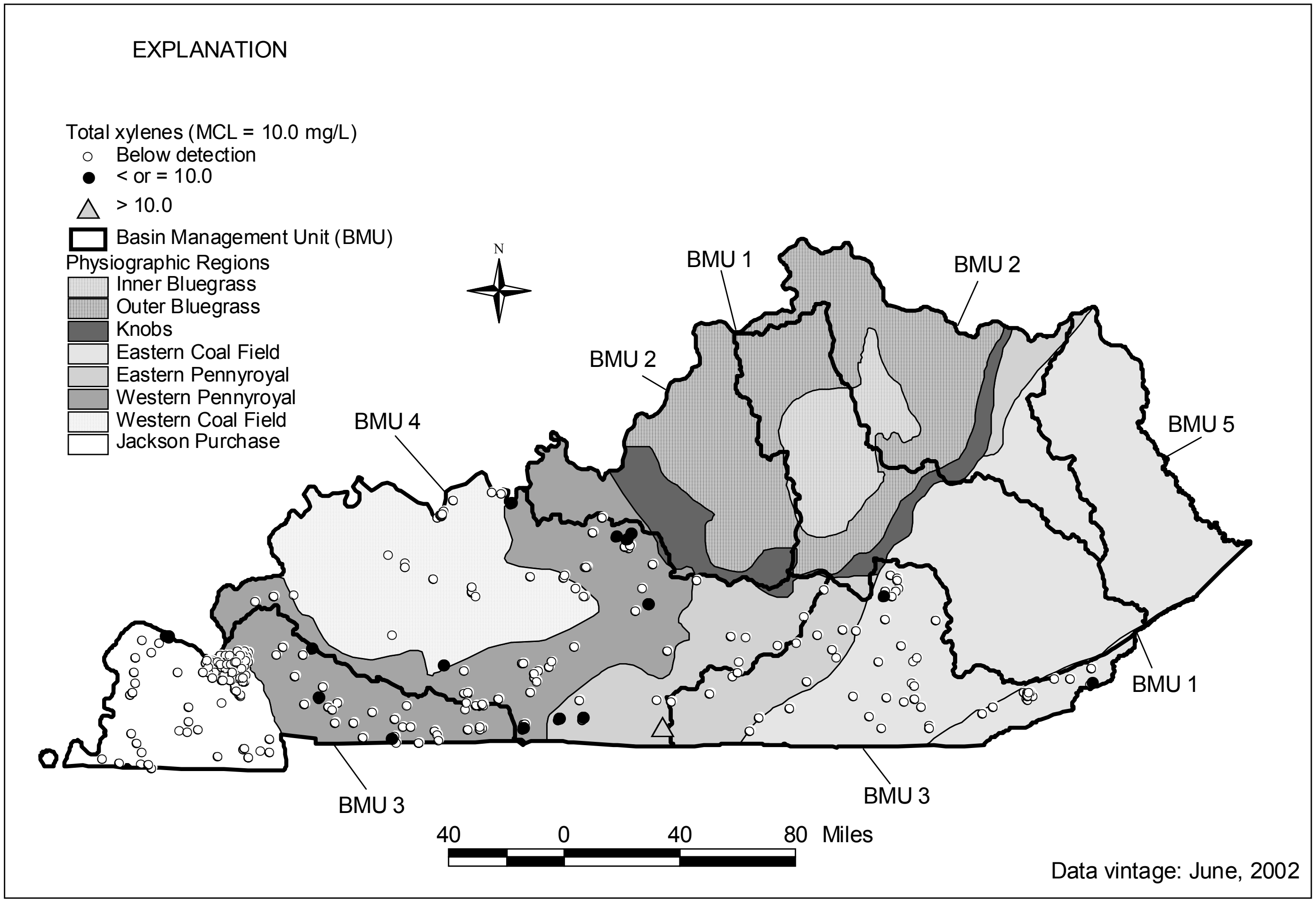


Figure 139. Map showing sample sites and total xylenes values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

MTBE (methyl tert-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, DOW has set a risk-based water-quality standard of 0.050 mg/L.

The data repository contained 551 MTBE measurements at 188 sites in BMU's 3 and 4 (Table 33). Thirty-two of the reported values were greater than analytical detection limits. Three sites in BMU 3 and 11 sites in BMU 4 produced water with detectable amounts of MTBE. Two springs and one well (130 ft deep) in BMU 4 had MTBE concentrations greater than the risk-based DEP standard (Fig. 140). No depths were reported with the MTBE data, so investigating MTBE concentrations as a function of well depth was not possible.

Table 33. Summary of MTBE measurements (mg/L).

	BMU 3	**BMU 4**
Measurements	329	222
Measurements above analytical detection limits	7	25
Sites	106	82
Sites above analytical detection limits	3	11
Sites above DEP limit	0	3
Maximum	0.00689	0.14
3rd quartile	< 0.001	0.0019
Median	< 0.001	< 0.001
1st quartile	< 0.001	< 0.001
Minimum	0.00051	0.00045

DEP = 0.05 mg/L

"<" indicates that the analysis result was less than the detection limit; the value of the detection limit follows the "<" symbol.

Summary: MTBE generally does not occur at detectable levels in water from wells and springs in the project area. With only two exceptions, sites where MTBE was detected are springs or shallow wells in the carbonate, karst terrane of the Eastern and Western Pennyroyal Regions.

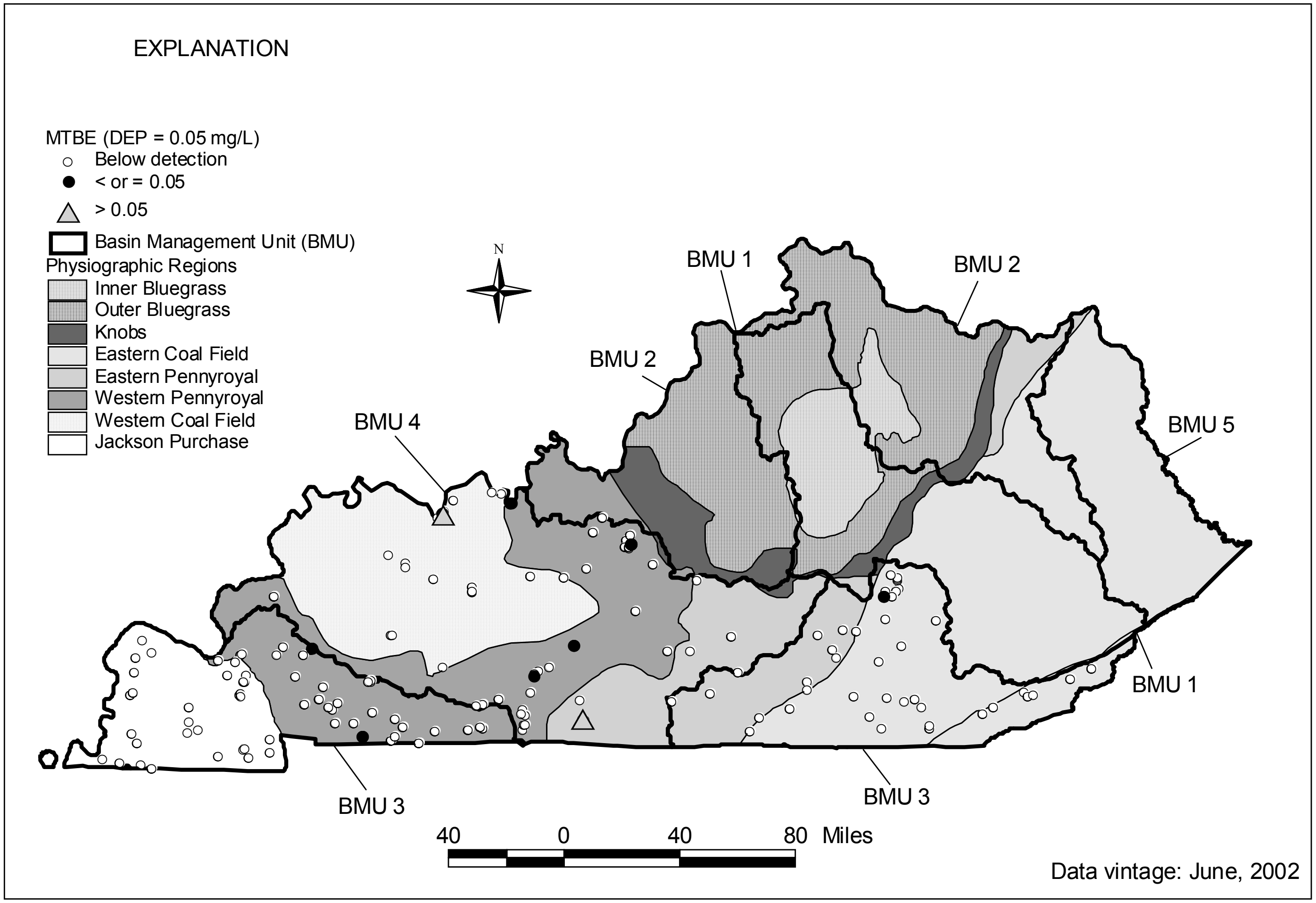


Figure 140. Map showing sample sites and MTBE values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

SUMMARY AND CONCLUSIONS

The goal of this project was to summarize and evaluate groundwater quality from basin management units 3 and 4 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 hundreds of wells and springs in Kentucky basin management units 3 (watersheds of the Upper and Lower Cumberland and Tennessee Rivers, and the Jackson Purchase) and 4 (watersheds of the Green and Tradewater Rivers) 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 are tabulated for each analyte. Probability plots and box and whisker diagrams are use to illustrate the data population, and the data are mapped to show sample site distribution.

The results show that the overall quality of Kentucky groundwater is good. However, there are many wells and springs where groundwater exceeds recommended levels for water properties, inorganic anions, metals, nutrients, pesticides, and volatile organic chemicals. 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 urban 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, it is known that pesticide levels in groundwater are highest following applications and after rainfall events. 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, it is likely that pesticides are 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 health effects at very low concentrations. The occurrence of volatile organic chemicals in groundwater is not natural and can only be the result of anthropogenic 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. Detections 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 BMU's 3 and 4.

	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	
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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